

DECLARATION

I, Mitsuru MAEDA, the translator of the attached document, do hereby certify that to the best of my knowledge and belief the attached document is a true English translation of Japanese Patent Application No. 2003-76650.

Signed, this 11th day of July, 2006

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METHOD FOR MANUFACTURING ELECTROPHOTOGRAPHIC PHOTORECEPTOR,
IMAGE FORMING APPARATUS AND PROCESS CARTRIDGE FOR IMAGE FORMING
APPARATUS

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【Title of the Invention】 ELECTROPHOTOGRAPHIC PHOTORECEPTOR, METHOD FOR MANUFACTURING ELECTROPHOTOGRAPHIC PHOTORECEPTOR, IMAGE FORMING APPARATUS AND PROCESS CARTRIDGE FOR IMAGE FORMING APPARATUS

【Claims】

【Claim 1】 An electrophotographic photoreceptor for use in an image forming apparatus in which an interval between light irradiation and developing is not longer than 100 ms, characterized by having a structure such that a photosensitive layer and a protective layer are overlaid on an electroconductive substrate, and a property such that a potential of a lighted portion of the photoreceptor changes at a rate of not greater than 700 V/sec not earlier than 35 msec after the light irradiation in the light irradiation-development interval.

【Claim 2】 The electrophotographic photoreceptor according to Claim 1, characterized in that the protective layer comprises at least a charge transport material.

【Claim 3】 The electrophotographic photoreceptor according to Claim 2, characterized in that the charge transport material is a charge transport polymer.

【Claim 4】 The electrophotographic photoreceptor according to Claim 3, characterized in that the charge transport polymer is a charge transport polymer having a triaryl amine skeleton.

【Claim 5】 A method for manufacturing an electrophotographic photoreceptor according to any one of Claims 1 to 4 by sequentially overlaying a photosensitive layer and a protective layer on an electroconductive substrate, characterized in that a solvent of a protective layer coating liquid includes a solvent, which can dissolve a resin included in the photosensitive layer, and the protective layer coating liquid is coated by a spray coating method, wherein the following relationship is satisfied:

【Equation 1】

$$1.3 < A/B < 1.9$$

wherein A represents a weight of the coated protective layer, which is measured after coating the protective layer coating liquid and allowing the coated liquid to settle for 1 hour; and B represents a weight of the coated protective layer, which is measured after coating the protective layer coating liquid and drying the coated liquid upon application of heat thereto.

【Claim 6】 An image forming apparatus comprising at least an electrophotographic photoreceptor, charging means, light irradiating means, developing means and transferring means, characterized in that the electrophotographic photoreceptor is an electrophotographic photoreceptor according to any one of Claims 1 to 4.

【Claim 7】 A process cartridge comprising at least an electrophotographic photoreceptor and at least one of charging means, light irradiating means, developing means, transferring means, cleaning means, and discharging means, characterized in that the electrophotographic photoreceptor is an electrophotographic photoreceptor according to any one of Claims 1 to 4.

【Detailed Description of the Invention】

【0001】

【Field of the Invention】

The present invention relates to an electrophotographic photoreceptor, a method for manufacturing the electrophotographic photoreceptor, and an electrophotographic image forming apparatus. The present invention's electrophotographic photoreceptor, image forming apparatus and process cartridge for image forming apparatuses can be applied to copiers, facsimiles, laser printers, direct digital plate making machines, etc.

【0002】

【Background Art】

In the past, photoreceptors using an inorganic photosensitive material such as selenium, zinc oxide and cadmium sulfide were mainly used as electrophotographic photoreceptors (hereinafter referred to as photoreceptors) for electrophotographic image forming apparatuses which are used for copiers and laser printers. However, at the present time organic photosensitive materials (OPCs) are broadly used because of having advantages of being friendly to global environment, and having low manufacturing costs and good designing flexibility over the inorganic photoreceptors.

【0003】

Organic photoreceptors are broadly classified into the following three types in view of layer structure:

- (1) homogeneous single-layered photoreceptors in which, for example, a photoconductive resin such as polyvinyl carbazole (PVK) or a charge transfer complex such as PVK-TNF (2,4,7-trinitrofluorenone) is formed on an electroconductive substrate;
- (2) dispersion type single-layered photoreceptors in which a resin layer including a pigment such as phthalocyanine and perylene, which is dispersed in the resin, is formed on an electroconductive substrate; and
- (3) functionally-separated multi-layered photoreceptors in which a charge generation layer (CGL) including a charge generation material such as azo pigments and a charge transport layer (CTL) including a charge transport material such as triphenyl amine are overlaid on an electroconductive substrate.

【0004】

The functionally-separated multi-layered photoreceptors

have a structure such that a charge transport layer is formed on a charge generation layer or an opposite structure such that the positions of the charge transport layer and the charge generation layer are reversed. Functionally-separated multi-layered photoreceptors having the latter structure are sometimes referred to as reverse-layered photoreceptors.

In particular, the functionally-separated multi-layered photoreceptors have advantages of having high photosensitivity and good flexibility in designing photoreceptors having high photosensitivity and good durability. Therefore, the recent functionally-separated multi-layered photoreceptors have this structure.

【0005】

In recent years, it is very important to manufacture products while considering influence thereof on the global environment. Therefore, photoreceptors to be used for image forming apparatus are required to serve as one of mechanical parts instead of a supply (i.e., a disposable product). In other words, photoreceptors are required to have a long life. Therefore, recent photoreceptors typically have a protective layer located on a photosensitive layer.

On the other hand, as for the toner for use in developing latent images formed by electrophotography, polymerized toners, spherical toners and small-sized toners (having a particle diameter of not greater than about 6 μm) have been mainly used because of being friendly to global environment in the manufacturing processes thereof and being able to produce high quality images. In order that photoreceptors have a good combination of cleanability and transferability even when such toners are used, the technique in that a protective layer is formed on the surfaces of photoreceptors attracts attention.

【0006】

The photoreceptors having a protective layer thereon often cause problems in that image qualities deteriorate due to formation of "a residual image" or "a ghost" of a previously formed image. In other words, at the present time there is no photoreceptor which has a good combination of durability or toner cleanability and image quality.

Particularly, in order to increase the printing speed of image forming apparatuses, the process speed has to be increased. Specifically, in high speed image forming apparatus such that the interval between the light irradiation process and the following development process is not greater than 100 msec, the residual images tend to be formed. Residual images are hardly formed in low- or medium-speed image forming apparatuses. (In the present application, high speed image forming apparatuses are defined as apparatuses in which the interval between the light irradiation process and the following development process is not greater than 100 msec.)

【0007】

The residual image phenomenon will be explained in detail.

When a half-tone image is formed after formation of an image which is constituted of only light image portions and dark image portions as illustrated in FIG. 14, there is a case where a residual image (positive or negative image) of the former image is observed in the half-tone image while highlighted, although the half-tone image has to be uniform. This is schematically illustrated in FIG. 15. The image is so called "a positive residual image" or "a positive ghost image". It is necessary to prevent formation of such deteriorated images, particularly in high quality full color image forming apparatuses. In contrast, there is a case where a residual image of the former image is observed in the half-tone image while having a low density. The image is called "a negative residual image" or "a negative

ghost image". It is also necessary to prevent formation of such deteriorated images. This is schematically illustrated in FIG. 16.

【0008】

The mechanism of formation of a residual image is considered to be caused by fluctuation of the surface potential of the photoreceptor as discussed in published unexamined Japanese Patent Application No. 11-133825 (patent document No. 1). The mechanism will be explained referring to FIG. 17, in which change of the potential of surface of a photoreceptor in the latent image forming process, developing process and transferring process is schematically illustrated.

【0009】

Referring to FIG. 17(a), in the latent image forming process the surface of a photoreceptor is charged so as to have a potential of -700 V and then exposed to imagewise light (the portion indicated by an arrow is a lighted portion). In this case, the potential of the lighted portion is about 0 V. Referring to FIG. 17(b), in the developing process development is performed by adhering a toner to the surface of the photoreceptor, wherein the amount of the adhered toner depends on the difference between the developing potential and the potential of the surface of the photoreceptor. Next, in the transfer process, the toner image on the photoreceptor is transferred onto a print sheet while positively charging the print sheet. When a reverse bias is applied to the photoreceptor by transfer means as illustrated in FIG. 17(c), the polarity of the potential of the lighted portions changes to a positive polarity (+10 V in FIG. 17(c)).

【0010】

When such a photoreceptor is uniformly charged negatively with charging means after these processes are repeatedly

performed, the surface potential of the portion of the photoreceptor, which was such a potential near the positive region before charging, also becomes a potential near the positive region. Therefore, difference between the surface potential of the portion and the development potential is higher than that in the other portions. Therefore, the portion is sensitized and thereby a dense toner image is formed. This image is observed as a positive residual image.

【0011】

As discussed in published unexamined Japanese patent application No. 2002-123067 (patent document No. 2), a residual image is also formed in a digital image forming method in which the image density of an image is changed by forming or not forming dot images (i.e., an image is formed by a binarization method) similarly to inkjet printing methods.

Specifically, the illuminance in a beam spot formed on a photoreceptor to form a latent dot image thereon is not uniform and has a certain distribution. When a beam spot is formed on the portion having a potential near the positive region, the developable latent dot image portion has a larger area than the other latent dot image portions because the potential of the latent dot image portion is offset toward the low potential side. Thus, the resultant dot toner image has a larger diameter than that of the dot image in other portions, and thereby the portions of the widened dot image portions are observed to be dense, resulting in formation of a residual positive image. This phenomenon is more prominent in high definition image formation with resolution of 1200 dpi than in image formation with resolution of 600 dpi. Namely, as the resolution of electrophotographic image forming apparatuses is enhanced, this problem becomes more serious.

【0012】

As discussed in published unexamined Japanese patent application No. 10-177261 (patent document No. 3), the main reason for the fluctuation of surface potential is considered to be that space charges are restored in the inside of a photoreceptor. Therefore, in order to prevent formation of a residual image, storage of space charges has to be prevented. In attempting to prevent storage of space charges, the following techniques have been disclosed.

【0013】

(1) Improvement of outermost layer of photoreceptor

Published unexamined Japanese patent application No. 10-115946 (patent document No. 4) discloses a photoreceptor having an outermost layer which includes a polyarylate resin and which has a dielectric constant of not less than 2.3. Since the mechanism thereof is under study, the mechanism is not described therein. However, it is clear from the examples that the effect is produced.

【0014】

Similarly to the proposal mentioned above, published unexamined Japanese patent application No. 11-184135 (patent document No. 5) discloses a photoreceptor having a photosensitive layer including an azo pigment and an outermost layer including a polyarylate resin. According to the publication, polyarylate resins have high crystallinity, and therefore can orient the charge transport material included therein to some extent. It is considered that by orienting a charge transport material and using a specific charge generation material (azo pigments), the charge injection barrier can be decreased and thereby the photo-memory property of the photoreceptor can be diminished.

【0015】

Published unexamined Japanese patent application No. 10-177263 (patent document No. 6) discloses that a multi-layered

photoreceptor having a charge generation layer including a phthalocyanine compound and an outermost layer including a bisphenol-based polycarbonate is used for an electrophotographic image forming apparatus having an intermediate transfer medium.

Although the mechanism thereof is not described therein, it is clear from the examples that the effect is produced. It is considered that the effect can be produced by using proper constitutional materials.

[0016]

Published unexamined Japanese patent application No. 10-177264 (patent document No. 7) discloses that a multi-layered photoreceptor having a charge generation layer including a phthalocyanine compound and an outermost layer including a charge transport polymer is used for an electrophotographic image forming apparatus having an intermediate transfer medium.

Although the mechanism thereof is not described therein, it is clear from the examples that the effect is produced. It is considered that the effect can be produced by using proper constitutional materials.

[0017]

Published unexamined Japanese patent application No. 10-177269 (patent document No. 8) discloses that a multi-layered photoreceptor having a charge generation layer including a phthalocyanine compound and either an insulative outermost layer or a semiconductive outermost layer including at least a resistance controlling agent is used for an electrophotographic image forming apparatus having an intermediate transfer medium.

Although the mechanism thereof is not described therein, it is clear from the examples that the effect is produced. It is considered that the effect can be produced by using proper constitutional materials.

【0018】

Published unexamined Japanese patent application No. 2000-147803 (patent document No. 9) discloses a photoreceptor in which a polycarbonate copolymer obtained from bisphenol A and a monomer having a specific arylene group is used for the outermost layer thereof such as charge transport layers. It is discussed in the publication that injection of charges having a reverse polarity from the outermost layer side can be prevented by using such a polycarbonate copolymer.

【0019】

Published unexamined Japanese patent application No. 2001-235889 (patent document No. 10) discloses a photoreceptor having an outermost layer including a surface-treated particulate metal oxide, an alcohol-soluble resin and an alcohol-soluble charge transport material. It is described in the publication that thermoplastic resins cannot be used as the binder resin of the outermost layer because the resins have insufficient mechanical strength, and since solvents used for forming the layer have to dissolve the resins used, the solvents also dissolve the photosensitive layer. Although the mechanism thereof is not described therein, it is considered from the examples that use of an alcohol-soluble charge transport material prevents formation of residual images.

【0020】

Published unexamined Japanese patent application No. 2002-6528 (patent document No. 11) discloses a photoreceptor having a photosensitive layer and a protective layer including at least one of an alkali metal element and an alkali earth metal element. It is considered that by including such an element in the protective layer, ionic conduction property can be imparted to the protective layer, and thereby good durability can be imparted to the photoreceptor while preventing storage

of residual charges. It is also described therein that it is possible to reduce residual charges by including a charge transport material in the protective layer but a problem such that the abrasion resistance of the protective layer deteriorates occurs.

【0021】

(2) Improvement of photosensitive layer

Published unexamined Japanese patent application No. 2000-75521 (patent document No. 12) discloses a photoreceptor including at least one of a chlorogarium phthalocyanine compound and a hydroxygarium phthalocyanine compound as a charge transport material and at least one of charge transport materials having a hydrazone skeleton. It is described in the publication that use of a good combination of a charge generation material and a charge transport material, which exchange charges, can diminish the transfer memory property and photo-memory property of the resultant photoreceptor. It is considered that since it is difficult to generalize good combinations of a charge generation material and a charge transport material at the present time, the above-mentioned combination is proper.

【0022】

Published unexamined Japanese patent application No. 2000-105478 (patent document No. 13) discloses a photoreceptor having a photosensitive layer including an azo pigment which is for use in an electrophotographic image forming apparatus using a laser diode emitting light with relatively short wavelength of from 380 to 500 nm as image writing light. Although the mechanism thereof is not described therein, it is considered from the examples that a number of azo pigments have relatively weak photo-memory property compared to α -form titanylphthalocyanine.

【0023】

Published unexamined Japanese patent application No. 2001-305762 (patent document No. 14) discloses a photoreceptor including a charge generation material and a charge transport material, wherein the charge transport material includes a first compound having a polarizability of greater than 70 Å which is calculated by structure optimizing calculation using semiempirical molecular orbital calculation using PM3 parameter and having a dipole moment less than 1.8D which is determined by calculation, and a second compound having 50% transmittance at a wavelength longer than the wavelength at which the first compound has 50% transmittance. It is considered that the second compound absorbs extra light irradiating the photoreceptor, and thereby the photo-memory property of the photoreceptor can be diminished.

【0024】

(3) Improvement of CTL

Published unexamined Japanese patent application No. 7-92701 (patent document No. 15) discloses a multi-layered photoreceptor in which an oxytitaniumphthalocyanine is included in the charge generation layer and at least two kinds of charge transport materials are included in the charge transport layer, wherein the difference in oxidation potential between the at least two kinds of charge transport materials is not greater than 0.04 V. The explanation of the mechanism is unclear, but it is considered that by using charge transport materials having almost the same energy level, hopping of the charge carriers between the charge transport materials can easily occur and the chance of trapping of charge carriers by the charge transport materials can be decreased, thereby decreasing the quantity of electrons excited by reverse charging performed by a transfer device, resulting in prevention of formation of a residual image.

【0025】

Published unexamined Japanese patent application No. 8-152721 (patent document No. 16) discloses a photoreceptor which is used for back-lighting type high speed image forming apparatus (in which the interval between light irradiation and development is from 10 to 150 msec), wherein the charge transport layer of the photoreceptor has a charge mobility of not less than $1 \times 10^{-6} \text{ cm}^2/\text{V} \cdot \text{sec}$ at an electric field strength of $2 \times 10^6 \text{ V/cm}$. It is described therein that when a photoreceptor has a low dynamic photosensitivity, the latent image formation cannot be completed before the start of a developing operation and thereby the potential of the former image portions is increased after repeated use. However, by using the technique mentioned above, the dynamic photosensitivity property can be improved and thereby formation of a residual image can be avoided.

【0026】

Published unexamined Japanese patent application No. 10-177262 (patent document No. 17) discloses a multi-layered photoreceptor which is for use in electrophotographic image forming apparatuses having an intermediate transfer medium and which has a charge generation layer including a phthalocyanine compound and a charge transport layer including a compound selected from triphenylamine compounds and N,N,N',N'-tetraphenylbenzidine compounds. Although the explanation of the mechanism is not described therein, it is clear from the examples that the effect is produced. It is considered that the effect can be produced by using proper constitutional materials.

【0027】

(4) Improvement of charge generation layer

Published unexamined Japanese patent application No. 6-313972 (patent document No. 18) discloses a photoreceptor in which the thickness of the charge generation layer is increased

so as to be not less than 25 μm or the content of a charge generation material in the charge generation layer is increased so as to be not less than 50 % by weight so that a number of charge carriers are trapped in the charge generation layer, to make the resultant ghost image invisible.

[0028]

Published unexamined Japanese patent application No. 10-69104 (patent document No. 19) discloses a multi-layered photoreceptor having a charge generation layer including a triarylamine compound having a xylol group. It is described in the publication that a barrier to carrier transportation is formed at the interface between the charge generation layer and charge transport layer, and charge carriers are trapped thereby. Since the trapped carriers decrease the space electric field in the charge generation layer, the potential of a half-tone image portion is not decreased, and thereby a residual image is formed at the portion. By including a charge transport material (i.e., a triarylamine compound having a xylol group) in the charge generation layer, the generated carriers are rapidly injected into the charge transport material and thereby the carriers are transported to the charge transport layer. Therefore, accumulation of trapped carriers can be prevented, resulting in prevention of occurrence of a residual image.

[0029]

Published unexamined Japanese patent application No. 10-186696 (patent document No. 20) discloses a photoreceptor having an electroconductive substrate and at least a photosensitive layer and a protective layer, which are located overlying the substrate in this order, wherein the photosensitive layer includes oxytitaniumphthalocyanine having an $\text{CuK}\alpha$ X-ray diffraction spectrum in which strong peaks are observed at Bragg (2θ) angles of 9.5° , 24.1° and 27.3° ($\pm 0.2^\circ$). Although the

explanation of the mechanism is not described therein, it is clear from the examples that the effect is produced. It is considered that the effect can be produced by using proper constitutional materials.

【0030】

Published unexamined Japanese patent application No. 2002-107972 (patent document No. 21) discloses a photoreceptor having a charge generation layer including a hydroxygarium phthalocyanine compound and a butyral resin which serves as the binder resin and which has an acetal group, an acetyl group and a hydroxyl group, wherein the butyral resin has a butyralation degree of not less than 62 % by mole, a weight average molecular weight (Mw) of not less than 2.0×10^5 and a number average molecular weight of not less than 5.0×10^4 . It is considered that the number of photo-carriers can be reduced by using the specific polyvinyl butyral (which is influenced by, for example, the number of hydroxyl groups therein), and thereby formation of a residual image can be prevented.

【0031】

(5) Improvement by matching charge generation layer with charge transport layer

Published unexamined Japanese patent application No. 7-43920 (patent document No. 22) discloses a multi-layered photoreceptor in which a specific azo pigment is used for the charge generation layer and a charge transport material having a fluorenone skeleton is used for the charge transport layer. Although the explanation of the mechanism is not described therein, it is clear from the examples that light fatigue preventing effect is produced. It is considered that the effect can be produced by using proper constituting materials.

【0032】

Published unexamined Japanese patent application No.

9-211876 (patent document No. 23) discloses a negative polarity-type photoreceptor having a high γ property, in which a charge generation layer including a phthalocyanine compound and a p-type charge transport layer including a material selected from the group consisting of inorganic p-type semiconductors, particulate t-Se and charge transport polymers are formed on an electroconductive substrate. It is described therein that the p-type charge transport layer is characterized by including no positive hole transport material and thereby diffusion of a positive hole transport material into the charge generation layer can be prevented. Therefore, trapping caused by the phthalocyanine pigment can be prevented and thereby formation of a residual image can be prevented.

[0033]

(6) Improvement of undercoat layer

Published unexamined Japanese patent application No. 8-22136 (patent document No. 24) discloses a photoreceptor having an undercoat layer prepared by using a silane coupling agent and an inorganic filler. It is described therein that by forming such an undercoat layer, charges to be flown to the substrate are smoothly flown to the substrate, and thereby formation of a residual image can be prevented.

[0034]

Published unexamined Japanese patent application No. 11-184127 (patent document No. 25) discloses a photoreceptor having an undercoat layer (an intermediate layer) including a resin having a specific polyamide acid or a polyamide acid ester structure, a polyimide resin having a specific polyimide structure, and a resin having a cyanoethyl group. Although the mechanism is not described therein, it is clear from the examples that the light fatigue preventing effect is produced. It is considered that the effect is produced by using proper materials.

【0035】

Published unexamined Japanese patent application No. 2000-112162 (patent document No. 26) discloses a photoreceptor having an undercoat layer (an intermediate layer) including a crosslinking resin which hardly changes its resistance even when the environmental humidity changes. It is described therein that published unexamined Japanese patent application No. 8-146639 discloses an undercoat layer including a polycyclic quinone, perylene, etc.; published unexamined Japanese patent application No. 10-73942 discloses an undercoat layer including a metallocene compound, an electron accepting compound and a melamine resin; published unexamined Japanese patent application No. 8-22136 discloses an undercoat layer including a particulate metal oxide and a silane coupling agent; and published unexamined Japanese patent application No. 9-258469 discloses an undercoat layer including a particulate metal oxide having a surface treated with a silane coupling agent.

It is described therein that in a highly sensitive photoreceptor including oxytitanium phthalocyanine in its charge generation layer, a large number of molecules and carriers are excited, and therefore a large number of molecules which do not cause charge separation and a large number of electrons and holes tend to remain in the photoreceptor in an electrophotographic process in which charging and light irradiating are repeated.

In attempting to solve the problem, the publication proposes to use a combination of a polyamide resin and a zirconium compound or a combination of a polyamide resin, a zirconium alkoxide and a diketone compound such as acetyl acetone for the undercoat layer. In addition, published unexamined Japanese patent application No. 2001-51438 (patent document No. 27) proposes to use a combination of a cellulose resin, a zirconium

compound, a zirconium alkoxide, and a diketone compound for the undercoat layer.

【0036】

Published unexamined Japanese patent application No. 2001-305763 (patent document No. 28) discloses a photoreceptor having an undercoat layer, and including a charge generation material and a charge transport material, wherein the charge transport material includes a material having a polarizability greater than 70 Å which is calculated by structure optimizing calculation method utilizing semiempirical molecular orbital calculation using PM3 parameter and having a dipole moment less than 1.8D which is determined by calculation, and a specific arylamine compound, wherein the undercoat layer includes a particulate titanium oxide treated with an organic silicon compound and a polyaminide having a specific diamine component as a constituent. It is described therein that by forming the undercoat layer, the photo-memory property can be improved. The mechanism thereof is considered to be that by forming such an undercoat layer, the carriers remaining in the photosensitive layer can be easily transported.

【0037】

Published unexamined Japanese patent application No. 2002-107983 (patent document No. 29) discloses a system in which the undercoat layer of the photoreceptor has a volume average resistivity of from 10^{10} to 10^{12} $\Omega \cdot \text{cm}$, the charge transport layer thereof has a thickness not greater than 18 μm and the image forming apparatus does not include a discharger. It is considered that by not using a discharger, the photoreceptor is prevented from suffering light fatigue. In addition, since the undercoat layer has a proper resistance, injection of charges from the substrate to the photosensitive layer can be suppressed, resulting in prevention of accumulation of space charges in the

photoreceptor.

【0038】

(7) Addition of additives

Published unexamined Japanese patent application No. 10-177261 discloses a photoreceptor for use in an electrophotographic image forming apparatus having an intermediate transfer medium, wherein the photoreceptor has a charge generation layer including a phthalocyanine compound and an outermost layer including a material having a hindered phenol structure. Although the mechanism is not described therein, but it is clear from the examples that the effect is produced. It is considered that the effect is produced by using proper materials.

【0039】

Published unexamined Japanese patent application No. 2000-292946 (patent document No. 30) discloses a photoreceptor having a charge generation layer including a phthalocyanine pigment and a dithiobenzyl compound. Although the mechanism is not described therein, but it is clear from the examples that improvements are made in accumulation of photo-memory and formation of a positive ghost.

【0040】

(8) Improvement in image forming method

Published unexamined Japanese patent application No. 7-13374 (patent document No. 31) proposes a technique in that a photoreceptor is used after being charged reversely so as to have a reverse (positive) charge, and then the photoreceptor is allowed to settle.

In a photoreceptor having a high sensitive charge transport layer, a large number of charge carriers are induced by light irradiation. In this case, electrons whose number is the same as that of the holes injected to the charge transport layer are

formed. If the electrons are not discharged to the substrate, the electrons remain in the charge generation layer and thereby a residual image is formed. When such a photoreceptor is reversely (i.e., positively) charged, electrons are injected from the substrate and electron traps are formed in the charge generation layer. When light irradiation is performed on such a photoreceptor, difference in the number of electron traps between the lighted portions and non-lighted portions can be miniaturized, and thereby the ghost image is allowed to be invisible.

【0041】

Published unexamined Japanese patent application No. 7-44065 (patent document No. 32) discloses a technique in that a DC voltage overlapped with an AC voltage is applied to the substrate of the photoreceptor. By applying a reverse bias to the substrate, electrons trapped in the charge generation layer can be discharged therefrom. It is described therein that by overlapping an AC voltage, the electric current can be increased and thereby the reverse charge bias effect can be accelerated.

【0042】

Published unexamined Japanese patent application No. 10-123802 (patent document No. 33) discloses a technique in that charging (which is not a main charging) is performed on the multi-layered photoreceptor having a charge generation layer including a phthalocyanine compound and then light discharging is performed thereon, wherein the main charging is performed thereon if the predetermined portion of the photoreceptor reaches the main charging portion. It is described therein that by performing such an image forming method, the photoreceptor is charged after the space charges in the photoreceptor are released therefrom, and thereby formation of a residual image in initial image forming operations can be prevented.

【0043】

Published unexamined Japanese patent application No. 10-123855 (patent document No. 34) discloses a technique in that a controller is provided in an image forming apparatus, which controls the transfer current flowing from a transfer device to the multi-layered photoreceptor used, which has a charge generation layer including a phthalocyanine compound. It is described therein that the greater the transfer current, the more conspicuously a negative residual image is formed. The reason is considered as follows. When an image is transferred, holes (positive holes) are injected into non-lighted portions (non-image portions) of the photoreceptor and the holes are trapped at the charge generation layer or the interface of the charge transport layer on the substrate side. The trapped holes are released in the next charging process, and thereby the dark decay is enhanced (i.e., apparent sensitization), resulting in occurrence of formation of a negative residual image. Therefore, by controlling the transfer current, the number of charge carriers injected into the photoreceptor can also be controlled and formation of a residual image can be prevented.

【0044】

Published unexamined Japanese patent application No. 2000-231246 (patent document No. 35) proposes a technique in that the wavelength of the image writing light and the discharging light are determined depending on the action spectrum representing the ratio of photo-memory property before charging to the photosensitivity of the photoreceptor.

【0045】

Published unexamined Japanese patent application No. 10-123856 (patent document No. 36) proposes a technique in that light irradiation is performed on a photoreceptor having a charge generation layer including a phthalocyanine compound before a

transfer process to decrease the potential of the non-lighted portion to 1/3 of the potential, in order to prevent formation of a residual image. The mechanism is not described therein but it is considered that by performing such irradiation before transferring, the difference in potential between the lighted portion and the non-lighted portion can be decreased and thereby the residual image can be made invisible.

[0046]

Published unexamined Japanese patent application No. 10-246997 (patent document No. 37) discloses a technique in that in an image forming apparatus using a photoreceptor having a photosensitive layer and a protective layer including a light-curable acrylic resin, a humidity sensor is provided in the vicinity of the photoreceptor to change the current of the AC component of the voltage applied by the charger depending on the humidity. In the publication, the mechanism of decrease of chance of formation of blurred images by providing the humidity sensor is described, but the mechanism why the photo-memory property of the photoreceptor is weakened is not described. However, it can be confirmed from the examples that the photo-memory property of the photoreceptor is weakened using the humidity sensor.

[0047]

Published unexamined Japanese patent application No. 2001-117244 (patent document No. 38) discloses a technique in that in order to prevent formation of a ghost image when a S-form photoreceptor is used, the period of half-decay of the potential on the photoreceptor in the light irradiation process, which period is determined using a Xerographic Time Of Flight (TOF) method, is controlled so as to be not greater than 1/10 of the interval between the light irradiation process and the following development process (hereinafter sometimes referred to as

exposure-development interval) in the electrophotographic image forming apparatus.

【0048】

As described in the paragraph in which the undercoat layer is improved, published unexamined Japanese patent application No. 2002-107983 discloses a technique in that by not using a discharger, the photoreceptor is prevented from suffering light fatigue.

【0049】

Published unexamined Japanese patent application No. 2002-123067 (patent document No. 39) discloses a technique in that the photoreceptor and charging conditions are controlled so as to satisfy the following relationship:

$$|(V1 - V2)/VH| < 0.020$$

wherein VH represents the potential of the charged photoreceptor; V1 represents the potential of the photoreceptor after a dark decay for a time of 10T, wherein T represents the charge-exposure interval; and V2 represents the potential of the photoreceptor after a dark decay for a time of 10 T, which photoreceptor is charged after one cycle of charging and light irradiation has been completed.

Specifically, a method in which the process speed is increased to shorten the dark decay time or the charge potential of the photoreceptor is lowered is proposed as the practical method.

【0050】

The above-mentioned prior techniques were applied to prevent photoreceptors having a photosensitive layer and a protective layer from forming residual images. As a result, it is found that the techniques cannot be satisfactorily used for photoreceptors and image forming apparatuses which have good durability and can produce high quality images at a high speed.

In addition, it is discovered that when a protective layer is formed on a commercialized photoreceptor which does not form a residual image, the resultant photoreceptor forms a residual image. Therefore the cause for a residual image is considered to lie in the protective layer.

Accordingly, it is considered that even if the techniques mentioned above in paragraphs (2) to (7) are applied to a photoreceptor having a protective layer, the residual image improving effect is little. In addition, if the technique mentioned above in paragraph (8) is applied, the resultant image forming apparatus has one or more of the drawbacks such that the image quality is not uncompromising quality; the image forming apparatus becomes large in size; the print costs including maintenance costs increase; and devices not satisfying the user's needs have to be used. Therefore the apparatus cannot be commercialized.

Further, the technique mentioned above in paragraph (1) relates to photoreceptors having no protective layer, and therefore even when the technique is applied to photoreceptors having a protective layer, the expected effect cannot be produced. When the other techniques are applied, there is a case where the effect can be hardly produced depending on the properties of the photoreceptor such as the thickness of the outermost layer of the photoreceptor. In addition, there is a case where the effects produced by forming a protective layer (such as impartment of high durability, good cleanability and good transferability) wear off when such techniques are applied.

Thus, the residual image problem cannot be fully solved by the conventional techniques.

【0051】

【Patent document No. 1】

Published unexamined Japanese patent application No.

11-133825

【Patent document No. 2】

Published unexamined Japanese patent application No.

2002-123067

【Patent document No. 3】

Published unexamined Japanese patent application No.

10-177261

【Patent document No. 4】

Published unexamined Japanese patent application No.

10-115946

【Patent document No. 5】

Published unexamined Japanese patent application No.

11-184135

【Patent document No. 6】

Published unexamined Japanese patent application No.

10-177263

【Patent document No. 7】

Published unexamined Japanese patent application No.

10-177264

【Patent document No. 8】

Published unexamined Japanese patent application No.

10-177269

【Patent document No. 9】

Published unexamined Japanese patent application No.

2000-147803

【Patent document No. 10】

Published unexamined Japanese patent application No.

2001-235889

【Patent document No. 11】

Published unexamined Japanese patent application No.

2002-6528

【Patent document No. 12】

Published unexamined Japanese patent application No.
2000-75521
【Patent document No. 13】
Published unexamined Japanese patent application No.
2000-105478
【Patent document No. 14】
Published unexamined Japanese patent application No.
2001-305762
【Patent document No. 15】
Published unexamined Japanese patent application No.
7-92701
【Patent document No. 16】
Published unexamined Japanese patent application No.
8-152721
【Patent document No. 17】
Published unexamined Japanese patent application No.
10-177262
【Patent document No. 18】
Published unexamined Japanese patent application No.
6-313972
【Patent document No. 19】
Published unexamined Japanese patent application No.
10-69104
【Patent document No. 20】
Published unexamined Japanese patent application No.
10-186696
【Patent document No. 21】
Published unexamined Japanese patent application No.
2002-107972
【Patent document No. 22】
Published unexamined Japanese patent application No.
7-43920

【Patent document No. 23】

Published unexamined Japanese patent application No.
9-211876

【Patent document No. 24】

Published unexamined Japanese patent application No.
8-22136

【Patent document No. 25】

Published unexamined Japanese patent application No.
11-184127

【Patent document No. 26】

Published unexamined Japanese patent application No.
2000-112162

【Patent document No. 27】

Published unexamined Japanese patent application No.
2001-51438

【Patent document No. 28】

Published unexamined Japanese patent application No.
2001-305763

【Patent document No. 29】

Published unexamined Japanese patent application No.
2002-107983

【Patent document No. 30】

Published unexamined Japanese patent application No.
2000-292946

【Patent document No. 31】

Published unexamined Japanese patent application No.
7-13374

【Patent document No. 32】

Published unexamined Japanese patent application No.
7-44065

【Patent document No. 33】

Published unexamined Japanese patent application No.

10-123802

【Patent document No. 34】

Published unexamined Japanese patent application No.

10-123855

【Patent document No. 35】

Published unexamined Japanese patent application No.

2000-231246

【Patent document No. 36】

Published unexamined Japanese patent application No.

10-123856

【Patent document No. 37】

Published unexamined Japanese patent application No.

10-246997

【Patent document No. 38】

Published unexamined Japanese patent application No.

2001-117244

【Patent document No. 39】

Published unexamined Japanese patent application No.

2002-123067

【0052】

【Problem to be Solved by the Invention】

The object of the present invention is to provide an electrophotographic photoreceptor which has a protective layer on the surface thereof and which can produce high quality images without forming a residual image while having good durability, good cleanability and good transferability. In addition, the object of the present invention is to provide a method for manufacturing the photoreceptor; and an image forming apparatus and a process cartridge for an image forming apparatus, which use the electrophotographic photoreceptor.

【0053】

【Means for Solving the Problem】

The present inventor discovers that formation of a residual image, which is often formed by photoreceptors having a protective layer can be prevented when images are formed on the photoreceptors at a low speed. Namely, the present inventor considers that whether a residual image is formed depends on the response speed of the photoreceptors in the potential decaying process.

When the light irradiation-development interval between light irradiation and development is shortened, the potential of lighted portions of general organic photoreceptors increases to some extent. With respect to the dependence of potential of a lighted portion on the light irradiation-development interval, a transition time at which the slope of the potential decay curve is changed is observed. Since the slope of the potential decay curve a short time side thereof is sharper than that at a long time side, the potential of the lighted portion rapidly increases if the light irradiation-development interval is shortened at the short time side.

The present inventor discovers that formation of a residual image closely relates to the time dependence of potential of a lighted portion of a photoreceptor. Specifically, it is discovered that when the time dependence of potential of a lighted portion is not greater than a specific value, formation of a residual image can be prevented. More specifically, it is discovered that when the change rate of potential of a lighted portion, which is measured while the light irradiation-development interval is changed, is not greater than 700V/sec, formation of a residual image can be prevented.

In addition, the present inventor considers that when a protective layer is formed on a photosensitive layer without dissolving the photosensitive layer, a barrier is formed between the photosensitive layer and the protective layer and charges

tend stay at the interface therebetween. In reality, when a protective layer is formed by coating a coating liquid on a photosensitive layer while dissolving the photosensitive layer to an extent not less than the predetermined extent, the photoreceptor can have a residual image improving effect. The present invention is made from this knowledge and consideration.

【0054】

Next, the method for evaluating the time dependence of the potential light decay property of a photoreceptor, which is the feature of the present invention will be explained.

Methods for evaluating the time dependence of the potential light decay property of a photoreceptor have been disclosed, for example, in published unexamined Japanese patent applications Nos. 10-115944 and 2001-312077. Namely, in the methods, the potential light decay property of a film of a charge transport material or a film constituted of a resin and a charge transport material is estimated by a Time Of Flight (TOF) method. These methods are useful when photoreceptors are designed. However, the charge transport conditions in practical image forming apparatus are different from those in the TOF method. Specifically, in practical image forming apparatus, the strength of the electric field formed on the film of a photoreceptor changes with time after a light irradiation process, whereas in the TOF method the strength of the electric field formed on the film of the photoreceptor is constant. In addition, the TOF method does not consider the influence of the charges generated in a charge generation layer due to light irradiation and the charges injected from a charge generation layer to a charge transport layer on charge transporting.

【0055】

A method by which the response of a photoreceptor is directly evaluated is disclosed in, for example, published

unexamined Japanese patent application No. 2000-305289. In the method, change of potential of a photoreceptor after light irradiation is recorded using a high speed surface potential meter to determine the time needed for the photoreceptor to have a predetermined potential. This method is called "Xerographic Time Of Flight (XTOF) method". Since this method remedies the drawbacks of the TOF method, the method is a useful evaluation method. However, the light source used for this method is often different from that used for the light irradiators of practical image forming apparatus. Therefore, the method is not necessarily a direct measuring method.

【0056】

Published unexamined Japanese patent application No. 2000-275872 discloses an apparatus for evaluating the characteristic of a photoreceptor. By using this apparatus, it becomes possible to determine the relationship between the potential of a lighted portion and time (i.e., light-decay curve) when the photoreceptor is exposed to light emitted by a laser diode (LD) while setting the time taken for moving a lighted portion to the developing means (hereinafter referred to as the light irradiation-development interval (Ted)). The light-decay curve of a photoreceptor is illustrated in FIG. 12.

When the potential of a lighted portion is plotted while the light irradiation-development interval is changed, a transition point at which the slope of the potential changes can be found. In this regard, the light irradiation-development interval at the transition point is hereinafter referred to as a transition time.

By using this method, the relationship between the light irradiation-development interval and the potential of the lighted portion, i.e., the time dependence of the potential light decay property of a photoreceptor can be precisely determined.

【0057】

The present inventor studies the relationship between the charge decay property of photoreceptors and image qualities such as instability of image density and formation of residual images using this evaluation method. As a result thereof, the following can be found.

【0058】

(1) Residual images are often formed when a photoreceptor is used under a condition such that the light irradiation-development interval is shorter than the transition time. In particular, when the image forming apparatus does not use a discharger, the tendency strengthens.

【0059】

(2) By decreasing the change of potential of a lighted portion at a time shorter than the transition time in the light irradiation-development interval, formation of a residual image can be prevented.

【0060】

(3) When the change of potential of a lighted portion (e.g., the slope illustrated in FIG. 13) from a time 35 msec after the exposure to the transition time is not greater than 700 V/sec, formation of a residual image can be prevented.

【0061】

(4) In order to decrease the change of potential of a lighted portion at a time shorter than the transition time, it is effective to include a charge transport material in the protective layer.

Even when a charge transport material is not included in the protective layer coating liquid, it is possible to include a charge transport material in the protective layer by forming the protective layer while dissolving the underlying photosensitive layer (a charge transport layer), resulting in formation of an unclear interface between the layers.

【0062】

From the above-mentioned knowledge, an electrophotographic photoreceptor and an electrophotographic image forming apparatus, which do not form uneven density images and residual images even when the image irradiation-development interval is shortened, can be provided.

【0063】

According to the present invention, (1) an electrophotographic photoreceptor for use in an image forming apparatus is provided in which the interval between light irradiation and developing is not longer than 100 ms and which is characterized by having a structure such that a photosensitive layer and a protective layer are overlaid on an electroconductive substrate, and a property such that a potential of a lighted portion of the photoreceptor changes at a rate of not greater than 700 V/sec not earlier than 35 msec after the light irradiation in the light irradiation-development interval.

【0064】

According to the present invention, (2) an electrophotographic photoreceptor is provided which accords with the photoreceptor mentioned above in paragraph (1) and which is characterized in that the protective layer includes at least a charge transport material (preferably a charge transport polymer, and more preferably a charge transport polymer having a triaryl amine skeleton).

【0065】

According to the present invention, (3) a method for manufacturing an electrophotographic photoreceptor mentioned above in paragraph (1) or (2) by sequentially overlaying a photosensitive layer and a protective layer on an electroconductive substrate is provided which is characterized in that the solvent of a protective layer coating liquid includes

a solvent, which can dissolve a resin included in the photosensitive layer, and the protective layer coating liquid is coated by a spray coating method, wherein the following relationship is satisfied:

$$1.3 < A/B < 1.9$$

wherein A represents a weight of the coated protective layer, which is measured after coating the protective layer coating liquid and allowing the coated liquid to settle for 1 hour; and B represents a weight of the coated protective layer, which is measured after coating the protective layer coating liquid and drying the coated liquid upon application of heat thereto.

【0066】

According to the present invention, (4) an image forming apparatus is provided which includes at least an electrophotographic photoreceptor, charging means, light irradiating means, developing means and transferring means and which is characterized in that the electrophotographic photoreceptor is an electrophotographic photoreceptor mentioned above in paragraph (1) or (2).

【0067】

According to the present invention, (5) a process cartridge is provided which includes at least an electrophotographic photoreceptor and at least one of charging means, light irradiating means, developing means, transferring means, cleaning means, and discharging means and which is characterized in that the electrophotographic photoreceptor is an electrophotographic photoreceptor mentioned above in paragraph (1) or (2).

【0068】

【Embodiments of the Invention】

Hereinafter the present invention will be explained in detail.

At first, the image forming apparatus of the present invention will be explained referring to drawings.

FIG. 1 is a schematic view for explaining the electrophotographic image forming apparatus of the present invention. The below-mentioned modified versions can also be included in the scope of the present invention.

In FIG. 1, a photoreceptor 11 is an electrophotographic photoreceptor which includes a photosensitive layer and a protective layer, which are located on an electroconductive substrate, wherein the potential of a lighted portion of the photoreceptor decreases at a rate of not greater than 700 V/sec not earlier than 35 msec after the light irradiation in the light irradiation-development interval.

The photoreceptor 11 has a drum form, but photoreceptors having another form such as sheet-form and endless belt-form as illustrated in FIG. 2 can also be used.

【0069】

As charging means 12, any known charging means such as corotrons, scorotrons, solidstate chargers, and rollerchargers can be used. Among the charging means, contact chargers and short-range chargers are preferably used because of consuming low power. In particularly, charging mechanisms which charge a photoreceptor while a proper gap is formed between the surface of the chargers and the surface of the photoreceptor are more preferably used because contamination of the charging means can be prevented.

【0070】

As transferring means 16, the above-mentioned known chargers can be used. Among the chargers, a combination of a transfer charger and a separation charger is preferably used.

【0071】

Suitable light sources for use in light irradiating means

13, discharging means 1A, etc. include all light emitting materials such as fluorescent lamps, tungsten lamps, halogen lamps, mercury lamps, sodium lamps, light emitting diodes (LEDs), laser diodes (LDs), and light sources using electroluminescence (EL). In addition, in order to obtain light having a desired wave length range, filters such as sharp-cut filters, band pass filters, near-infrared cutting filters, dichroic filters, interference filters, and color temperature converting filters can be used.

【0072】

When the image of a toner 15 formed on the photoreceptor 11 by developing means 14 is transferred onto a receiving material 18, all of the toner image are not transferred on the receiving material 18, and toner particles remain on the surface of the photoreceptor 11. The residual toner is removed from the photoreceptor 11 by cleaning means 17. As the cleaning means 17, cleaning blades made of a rubber, and brushes such as fur blushes and mag-fur blushes, etc. can be used.

【0073】

When the photoreceptor 11 which is previously charged positively (or negatively) is exposed to imagewise light, an electrostatic latent image having a positive (or negative) charge is formed on the photoreceptor 11. When the latent image having a positive (or negative) charge is developed with a toner having a negative (or positive) charge, a positive image can be obtained. In contrast, when the latent image having a positive (negative) charge is developed with a toner having a positive (negative) charge, a negative image can be obtained. Known developing means can be used as the developing means. In addition, known discharging means can also be used as the discharging means.

【0074】

FIG. 2 illustrates another embodiment of the image forming

process of the present invention. In FIG. 2, the photoreceptor 11 is an electrophotographic photoreceptor which includes a photosensitive layer and a protective layer, which are located on an electroconductive substrate, wherein the potential of a lighted portion of the photoreceptor decreases at a rate of not greater than 700 V/sec not earlier than 35 msec after the light irradiation in the light irradiation-development interval.

【0075】

The photoreceptor 11 is driven by driving means 1C. The photoreceptor 11 is repeatedly subjected to charging with the charging means 12, light irradiation with the light irradiating means 13, developing (not shown), transferring with the transferring means 16, pre-cleaning light irradiation with pre-cleaning light irradiation means, cleaning with the cleaning means 17 and discharging with the discharging means 1A. In the embodiment illustrated in FIG. 2, the pre-cleaning light irradiation process is performed by irradiating the photoreceptor 11 (whose substrate is light-transmissive in this case) with light from the side of the substrate thereof.

【0076】

The image forming apparatus of the present invention is not limited to the embodiments mentioned above, and other embodiments can be used. For example, in FIG. 2, the pre-cleaning light irradiating operation is performed from the substrate side, but can be performed from the photosensitive layer side of the photoreceptor 11. In addition, other than the light irradiation in the imagewise light irradiating process, pre-cleaning light irradiation process and discharging process, pre-transfer light irradiation, pre-imagewise light irradiation and other light irradiation may be performed on the photoreceptor.

【0077】

The above-mentioned image forming means may be fixedly

set in image forming apparatus such as copiers, facsimiles and printers. However, the image forming means may be set therein as a process cartridge. The process cartridge means a device (part), which includes a photoreceptor and at least one of charging means, light irradiating means, developing means, transferring means, cleaning means, and discharging means. Various types of process cartridges can be used in the present invention. An embodiment of the process cartridge of the present invention is illustrated in FIG. 3. In this case, the photoreceptor 11 is an electrophotographic photoreceptor which includes a photosensitive layer and a protective layer, which are located on an electroconductive substrate, wherein the potential of a lighted portion of the photoreceptor decreases at a rate of not greater than 700 V/sec not earlier than 35 msec after the light irradiation in the light irradiation-development interval. Although the photoreceptor 11 has a drum-form, photoreceptors having another form such as sheet-form and endless belt-form can also be used therefor.

【0078】

FIG. 4 illustrates another embodiment of the image forming apparatus of the present invention. In the image forming apparatus illustrated in FIG. 4, the charging means 12, the light irradiating means 13, developing means 14Bk, 14C, 14M and 14Y for black, cyan, magenta and yellow color toners, respectively, an intermediate transfer belt 1F, and the cleaning means 17 are arranged around the photoreceptor 11. In this regard, the suffixes Bk, C, M and Y mean the colors of the toners. The suffixes are sometimes omitted. The photoreceptor 11 is an electrophotographic photoreceptor which includes a photosensitive layer and a protective layer, which are located on an electroconductive substrate, wherein the potential of a lighted portion of the photoreceptor decreases at a rate of not

greater than 700 V/sec not earlier than 35 msec after the light irradiation in the light irradiation-development interval.

【0079】

The developing means 14Bk, 14C, 14M and 14Y can be independently controlled, and only one of the developing means corresponding to the color of the image to be formed is driven. Toner images formed on the photoreceptor 11 are transferred onto the intermediate transfer belt 1F by first transfer means 1D, which is arranged inside the intermediate transfer belt 1F. Since the first transfer means 1D is detachably attached to the photoreceptor 11, the intermediate transfer belt 1F is brought into contact with the photoreceptor 11 by the first transfer device 1D only when a transfer operation is performed. By sequentially performing each color image transferring, the toner images are overlaid on the intermediate transfer belt 1F. The thus obtained toner images are transferred onto the receiving material 18 at the same time by second transferring means 1E, and the toner images are then fixed on the receiving material 18 by fixing means 19. Thus, an image is formed. The second transferring means 1E is arranged so as to be detachably attached to the intermediate transfer belt 1F, and is brought into contact with the intermediate transfer belt 1F only when a transfer operation is performed.

【0080】

In an image forming apparatus using a drum transfer method, color toner images are transferred one by one onto a receiving material electrostatically attached to a transfer drum. Therefore, images cannot be formed on thick papers. However, in the image forming apparatus as illustrated in FIG. 4, each toner image is transferred on the intermediate transfer belt 1F to be overlaid thereon. Therefore, the image forming apparatus has an advantage in that the receiving material is

not particularly limited. This intermediate transfer-type image forming method can be applied to the image forming apparatus as illustrated in FIGS. 1-3, and 5 (specific example is illustrated in FIG. 6) as well as the image forming apparatus illustrated in FIG. 4.

【0081】

FIG. 5 illustrates another embodiment of the image forming apparatus of the present invention.

This image forming apparatus includes four image forming sections using respective color toners, i.e., yellow, magenta, cyan and black toners. The image forming sections include respective photoreceptors 11Y, 11M, 11C and 11Bk. The photoreceptor 11 used for the image forming apparatus is an electrophotographic photoreceptor which includes a photosensitive layer and a protective layer, which are located on an electroconductive substrate, wherein the potential of a lighted portion of the photoreceptor decreases at a rate of not greater than 700 V/sec not earlier than 35 msec after the light irradiation in the light irradiation-development interval.

【0082】

Around each of the photoreceptors 11Y, 11M, 11C or 11Bk, the charging means 12, light irradiating means 13, developing means 14, cleaning means 17, etc. are arranged. In addition, a feed/transfer belt 1G, which serves as a transfer material support and which is detachably attached to the linearly arranged photoreceptors at the transfer positions, is tightly stretched by driving means 1C. Transferring means 16 are arranged at the transfer positions at which the transferring means face the respective photoreceptors 1Y, 1M, 1C and 1Bk with the feed/transfer belt 1G therebetween.

【0083】

The tandem-type image forming apparatus illustrated in

FIG. 5 has a plurality of photoreceptors 1Y, 1M, 1C and 1Bk for forming four color images. Color toner images are sequentially transferred onto the receiving material 18 borne on the feed/transfer belt 1G. Therefore, the image forming apparatus can form full color images at a much higher speed than that of image forming apparatuses having only one photoreceptor.

【0084】

Next, the organic photoreceptor of the present invention will be explained in detail referring to drawings.

FIG. 7 illustrates a schematic cross section of an embodiment of the photoreceptor of the present invention. The photoreceptor has an electroconductive substrate 21, and a photosensitive layer 22 and a protective layer 23, which are overlaid on the electroconductive substrate 21.

FIG. 8 illustrates a schematic cross section of another embodiment of the photoreceptor of the present invention. The photoreceptor has an undercoat layer 24, which is located between the electroconductive substrate 21 and the photosensitive layer 22.

FIG. 9 illustrates a schematic cross section of another embodiment of the photoreceptor of the present invention. In the photoreceptor, a charge generation layer 25 and a charge transport layer 26 are provided.

FIG. 10 illustrates a schematic cross section of another embodiment of the photoreceptor of the present invention. The photoreceptor has the undercoat layer 24, which is located between the electroconductive substrate 21 and the charge generation layer 25.

【0085】

Suitable materials for use in the electroconductive substrate 21 include materials having a volume resistance not greater than $10^{10} \Omega \cdot \text{cm}$. Specific examples of such materials

include plastic cylinders, plastic films or paper sheets, on the surface of which is coated with a metal such as aluminum, nickel, chromium, nichrome, copper, gold, silver, platinum, iron and the like, or a metal oxide such as tin oxides, indium oxides and the like, by a method such as vapor deposition and sputtering. In addition, a plate of a metal such as aluminum, aluminum alloys, nickel and stainless steel can be used. A metal cylinder can also be used as the substrate 21, which is prepared by tubing a metal such as aluminum, aluminum alloys, nickel and stainless steel by a method such as drawing ironing, impact ironing, extruded ironing, extruded drawing or cutting, and then subjecting the surface of the tube to cutting, super finishing, polishing and the like treatments.

【0086】

In the photoreceptor of the present invention, the photosensitive layer 22 may be a mixture type photosensitive layer in which both a charge generation material and a charge transport material are dispersed, or a multi-layered photosensitive layer having a charge generation layer including a charge generation material, and a charge transport layer including a charge transport material, which are overlaid.

At first, the multi-layered photosensitive layer will be explained.

【0087】

At first, the charge generation layer 25 will be explained. The charge generation layer includes a charge generation material as a main component, and optionally includes a binder resin. Both of inorganic charge generation materials and organic charge generation materials can be used as the charge generation material.

【0088】

Specific examples of the inorganic charge generation

materials include crystalline selenium, amorphous selenium, selenium-tellurium compounds, selenium-tellurium-halogen compounds, selenium-arsenic compounds, amorphous silicon, etc. Among amorphous silicon, amorphous silicon in which a dangling bond is terminated with a hydrogen atom or a halogen atom or in which a boron atom, a phosphorous atom, etc. is doped is preferably used.

【0089】

Specific examples of the organic charge generation materials include phthalocyanine pigments such as metal phthalocyanine and metal-free phthalocyanine; azulenium salt type pigments; squaric acid methyne pigments; azo pigments having a carbazole skeleton; azo pigments having a triphenyl amine skeleton; azo pigments having a diphenyl amine skeleton; azo pigments having a dibenzothiophene skeleton; azo pigments having a fluorenone skeleton; azo pigments having an oxadiazole skeleton; azo pigments having a bisstilbene skeleton; azo pigments having a distyryloxadiazole skeleton; azo pigments having a distyrylcarbazole skeleton; perylene pigments, anthraquinone pigments, polycyclic quinone pigments, quinone imine pigments, diphenylmethane pigments, triphenylmethane pigments, benzoquinone pigments, naphthoquinone pigments, cyanine pigments, azomethine pigments, indigoide pigments, benzimidazole pigments, etc.

【0090】

These charge generation materials can be used alone or in combination.

【0091】

Specific examples of the binder resins, which are optionally included in the charge generation layer, include polyamide, polyurethane, epoxy resins, polyketone, polycarbonate, polyarylate, silicone resins, acrylic resins,

polyvinyl butyral, polyvinyl formal, polyvinyl ketone, polystyrene, poly-N-vinylcarbazole, polyacrylamide, etc.

These resins can be used alone or in combination.

【0092】

In addition, charge transport polymers can be used as the binder resin of the charge generation layer. Further, low molecular weight charge transport materials can be added to the charge generation layer if desired.

Charge transport materials for use in the charge generation layer are classified into positive-hole transport materials and electron transport materials. In addition, charge transport materials can be classified into low molecular weight charge transport materials and high molecular weight charge transport materials. In the present application, high molecular weight charge transport materials are referred to as charge transport polymers.

【0093】

Specific examples of the electron transport materials include electron accepting materials such as chloranil, bromanil, tetracyanoethylene, tetracyanoquinodimethane, 2,4,7-trinitro-9-fluorenone, 2,4,5,7-tetranitro-9-fluorenone, 2,4,5,7-tetranitroxanthone, 2,4,8-trinitrothioxanthone, 2,6,8-trinitro-4H-indeno[1,2-b]thiophene-4-one, 1,3,7-trinitrobenzothiophene-5,5-dioxide, and the like.

These electron transport materials can be used alone or in combination.

【0094】

Specific examples of the positive-hole transport materials include oxazole derivatives, oxadiazole derivatives, imidazole derivatives, triphenyl amine derivatives, 9-(p-diethylaminostyryl)anthracene, 1,1-bis-(4-dibenzylaminophenyl)propane, styryl anthracene,

styryl pyrazoline, phenyl hydrazone, α -phenyl stilbene derivatives, thiazole derivatives, triazole derivatives, phenazine derivatives, acridine derivatives, benzofuran derivatives, benzimidazole derivatives, thiophene derivatives, etc.

These positive hole transport materials can be used alone or in combination.

【0095】

Then the charge transport polymers for use in the photoreceptor of the present invention will be explained. Specific examples of the charge transport polymers are following polymers.

【0096】

(a) Polymers having a carbazole ring

Specific examples of such materials include poly-N-vinyl carbazole, and the compounds disclosed in published unexamined Japanese patent applications Nos. 50-82056, 54-9632, 54-11737, 4-175337, 4-183719 and 6-234841.

【0097】

(b) polymers having a hydrazone skeleton

Specific examples of such materials include the compounds disclosed in published unexamined Japanese patent applications Nos. 57-78402, 61-20953, 61-296358, 1-134456, 1-179164, 3-180851, 3-180852, 3-50555, 5-310904 and 6-234840.

【0098】

(c) Polysilylene compounds

Specific examples of such polymers include the polysilylene compounds disclosed in published unexamined Japanese patent applications Nos. 63-285552, 1-88461, 4-264130, 4-264131, 4-264132, 4-264133 and 4-289867.

【0099】

(d) Polymers having a triaryl amine skeleton

Specific examples of such polymers include N,N-bis (4-methylphenyl)-4-aminopolystyrene, and the compounds disclosed in published unexamined Japanese patent applications Nos. 1-134457, 2-282264, 2-304452, 4-133065, 4-133066, 5-40350 and 5-202135.

【0100】

(e) Other polymers

Specific examples of such polymers include condensation products of nitropyrene with formaldehyde, and the compounds disclosed in published unexamined Japanese patent applications Nos. 51-73888, 56-150749, 6-234836 and 6-234837.

【0101】

The polymer having an electron donating group for use in the present invention is not limited thereto, and copolymers, block copolymers, graft copolymers and star polymers, which are obtained from one or more known monomers, can also be used. In addition, crosslinking polymers having an electron donating group disclosed in, for example, published unexamined Japanese patent application No. 3-109406, can also be used.

【0102】

Among these charge transport materials, compounds having a triaryl amine structure are preferably used. Specific examples of such compounds have been disclosed in published unexamined Japanese patent applications Nos. 64-1728, 64-13061, 64-19049, 4-11627, 4-225014, 4-230767, 4-320420, 5-232727, 7-56374, 9-127713, 9-222740, 9-265197, 9-211877 and 9-304956.

【0103】

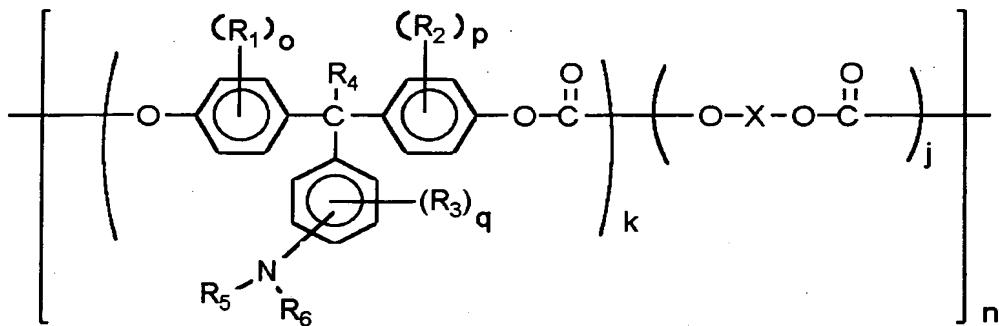
Specific examples of the charge transport polymers having a triarylamine structure, which can be preferably used for the photoreceptor of the present invention, include the following polymer materials. Charge transport materials having formulae 1 to 6 and specific examples thereof are described below.

【0104】

【Formula 1】

(formula 1)

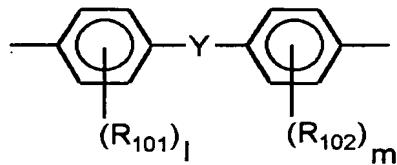
(一般式1)



【0105】

In the formula, R_1 , R_2 and R_3 independently represent a substituted or unsubstituted alkyl group, or a halogen atom; R_4 represents a hydrogen atom, or a substituted or unsubstituted alkyl group; R_5 , and R_6 represent a substituted or unsubstituted aryl group; o , p and q independently represent an integer of from 0 to 4; k and j represent a composition ratio and satisfy the following relationships, $0.1 \leq k \leq 1$ and $0 \leq j \leq 0.9$; n is the repeat number and is an integer of from 5 to 5000; and X represents a divalent aliphatic group, a divalent alicyclic group or a divalent group having the following formula:

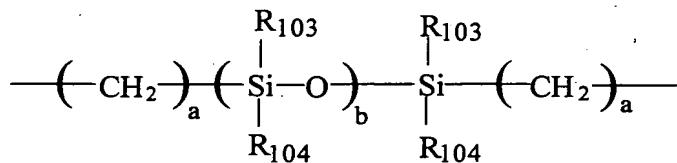
【Formula 2】



In the formula, R_{101} and R_{102} independently represent a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, or a halogen atom; l and m are an integer of from 0 to 4; and Y represents a single bond, a linear alkylene group, a branched alkylene group, a cyclic alkylene group, $-O-$,

-S-, -SO-, -SO₂-, -CO-, -CO-O-Z-O-CO- (Z represents a divalent aliphatic group), or a group having the following formula:

【Formula 3】



(In the formula, a is an integer of from 1 to 20; b is an integer of from 1 to 2000; and R₁₀₃ and R₁₀₄ represent a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group). In this regard, each of R₁₀₁ and R₁₀₂, and R₁₀₃ and R₁₀₄ may be the same or different from the other.

【0106】

[Specific examples of polymers having formula 1]

In the above-mentioned formula, R₁, R₂ and R₃ independently represent a substituted or unsubstituted alkyl group or a halogen atom. Specific examples thereof are as follows. The groups R₁, R₂ and R₃ may be the same as or different from the others.

【0107】

Suitable alkyl groups include linear or branched alkyl groups having from 1 to 12 carbon atoms, preferably from 1 to 8 carbon atoms and more preferably from 1 to 4 carbon atoms. These alkyl groups can be substituted with a halogen atom, a hydroxyl group, a cyano group, an alkoxy group having from 1 to 4 carbon atoms, a phenyl group, or a phenyl group which is substituted with an alkyl group having from 1 to 4 carbon atoms or an alkoxy group having from 1 to 4 carbon atoms.

Specific examples thereof include methyl groups, ethyl groups, n-propyl groups, i-propyl groups, t-butyl groups, s-butyl groups, n-butyl groups, i-butyl groups, trifluoromethyl groups, 2-hydroxyethyl groups, 2-cyanoethyl groups, 2-ethoxyethyl groups, 2-methoxyethyl groups, benzyl groups,

4-chlorobenzyl groups, 4-methylbenzyl groups, 4-methoxybenzyl groups, 4-phenylbenzyl groups, etc.

【0108】

Specific examples of the halogen atom include fluorine, chlorine, bromine and iodine atoms.

【0109】

R_4 represents a hydrogen atom, a substituted or unsubstituted alkyl group. Specific examples of the alkyl groups are the groups mentioned above for use in R_1 , R_2 and R_3 .

R_5 and R_6 represent a substituted or unsubstituted aryl group. Specific examples thereof include the following. The groups R_5 and R_6 may be the same as or different from the other.

【0111】

Specific examples of the aromatic hydrocarbon groups include phenyl groups, condensed ring groups (e.g., naphthyl groups, pyrenyl groups, 2-fluorenyl groups, 9,9-dimethyl-2-fluorenyl groups, azulenyl groups, anthryl groups, triphenylenyl groups, chrysenyl groups, fluorenylidene phenyl groups, and 5H-dibenzo[*a,d*] cycloheptenylidene phenyl groups), and non-condensed polycyclic ring groups (e.g., biphenylyl group, and terphenylyl groups).

【0112】

Specific examples of the heterocyclic ring groups include thienyl groups, benzothienyl groups, furyl groups, benzofuryl groups, and carbazolyl groups.

【0113】

The above-mentioned aryl groups can have a substituent. Specific examples of the substituent include the following groups.

【0114】

(1) Halogen atoms, trifluoromethyl groups, cyano groups and nitro

groups.

【0115】

(2) Alkyl groups mentioned above for use in R₁, R₂ and R₃.

【0116】

(3) Alkoxy groups (-OR₁₀₅). Specific examples of the group R₁₀₅ include the alkyl groups defined in numbered paragraph (2) above. Specific examples of the alkoxy groups include methoxy groups, ethoxy groups, n-propoxy groups, i-propoxy groups, t-butoxy groups, n-butoxy groups, i-butoxy groups, 2-hydroxyethoxy groups, 2-cyanoethoxy groups, benzyloxy groups, 4-methylbenzyloxy groups, trifluoromethoxy groups, etc.

【0117】

(4) Aryloxy groups. Specific examples of the aryl group of the aryloxy groups include phenyl groups, and naphthyl groups, which can have a substituent such as alkoxy groups having from 1 to 4 carbon atoms, alkyl groups having from 1 to 4 carbon atoms, and halogen atoms. Specific examples of the aryloxy groups include phenoxy groups, 1-naphthyoxy groups, 2-naphthyoxy groups, 4-methylphenoxy groups, 4-methoxyphenoxy groups, 4-chlorophenoxy groups, 6-methyl-2-naphthyoxy groups, etc.

【0118】

(5) Substituted mercapto groups and aryl mercapto groups. Specific examples thereof include methylthio groups, ethylthio groups, phenylthio groups, p-methylphenylthio groups, etc.

【0119】

(6) Amino groups substituted with an alkyl group. Specific examples of the alkyl groups are mentioned above in numbered paragraph (2) above. Specific examples of the substituted amino groups include dimethylamino groups, diethylamino groups, N-methyl-N-propylamino groups, N,N-dibenzylamino groups, etc.

【0120】

(7) Acyl groups. Specific examples of the acyl groups include

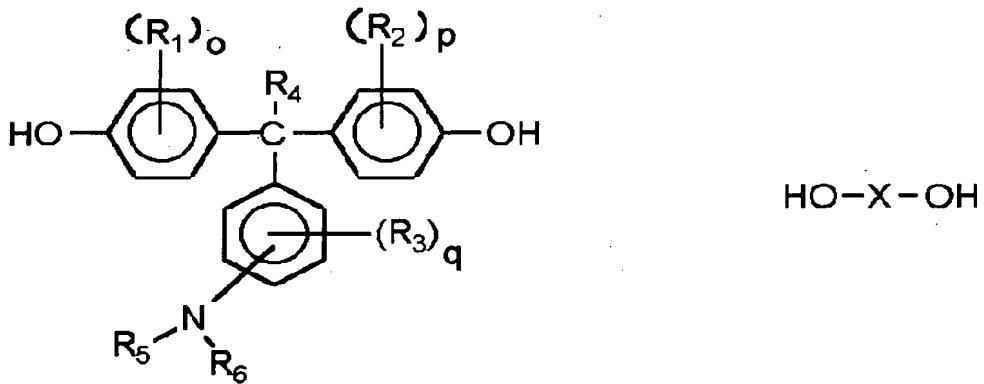
acetyl groups, propionyl groups, butylyl groups, malonyl groups, benzoyl groups, etc.

【0121】

The group X can be incorporated in the main chain of the polymers by polymerizing a diol compound having a triarylarnino group having the below-mentioned formula (A) together with a diol compound having the below-mentioned formula (B) using a method such as phosgene methods and ester exchange methods. In this case, the resultant polycarbonate resins are random or block copolymers. Alternatively, the group X can also be incorporated in the main chain by polymerizing the diol compound having formula (A) together with bischloroformate which can be derived from the diol compound having formula (B). In this case, the resultant polymers are alternating copolymers.

【0122】

【Formula 4】



Formula (A)

Formula (B)

【0123】

Specific examples of the diol compounds having formula (B) include aliphatic diols such as 1,3-propane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 1,8-octane diol, 1,10-decane diol, 2-methyl-1,3-propane diol,

2,2-dimethyl-1,3-propane diol, 2-ethyl-1,3-propane diol, diethylene glycol, triethylene glycol, polyethylene glycol, and polytetramethyleneether glycol; alicyclic diols such as 1,3-cyclohexane diol, and cyclohexane-1,4-dimethanol; etc.

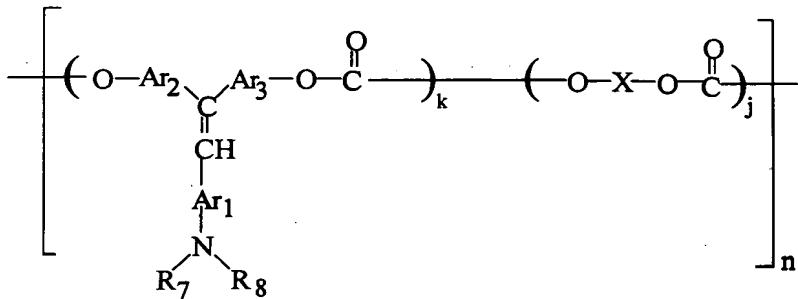
【0124】

In addition, diols having an aromatic ring can also be used. Specific examples thereof include 4,4-dihydroxydiphenyl, bis(4-hydroxyphenyl)methane, 1,1-bis(4-hydroxyphenyl)ethane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(3-methyl-4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 1,1-bis(4-hydroxyphenyl)cyclopentane, 2,2-bis(3-phenyl-4-hydroxyphenyl)propane, 2,2-bis(3-isopropyl-4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)butane, 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane, 4,4'-dihydroxydiphenylsulfone, 4,4'-dihydroxydiphenylsulfoxide, 4,4'-dihydroxydiphenylsulfide, 3,3'-dimethyl-4,4'-dihydroxydiphenylsulfide, 4,4'-dihydroxydiphenyloxide, 2,2-bis(4-hydroxyphenyl)hexafluoropropane, 9,9-bis(4-hydroxyphenyl)fluorenone, 9,9-bis(4-hydroxyphenyl)xanthene, ethyleneglycol-bis(4-hydroxybenzoate), diethyleneglycol-bis(4-hydroxybenzoate), triethyleneglycol-bis(4-hydroxybenzoate), 1,3-bis(4-hydroxyphenyl)tetramethyldisiloxane, phenol-modified silicone oils, etc.

【0125】

【Formula 5】

(formula 2)



【0126】

In the formula, R_7 and R_8 represent a substituted or unsubstituted aryl group; Ar_1 , Ar_2 and Ar_3 independently represent an arylene group; and X , k , j and n are defined above in formula 1.

【0127】

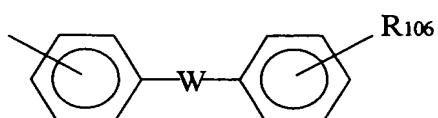
[Specific examples of polymers having formula 2]

Groups R_7 and R_8 represent a substituted or unsubstituted aryl group. Specific examples thereof are as follows. The groups R_7 and R_8 may be the same as or different from the other.

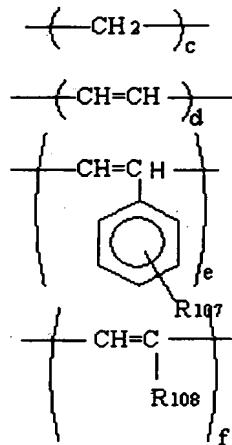
【0128】

Specific examples of the aromatic hydrocarbon groups include phenyl groups, condensed ring groups (e.g., naphthyl groups, pyrenyl groups, 2-fluorenyl groups, 9,9-dimethyl-2-fluorenyl groups, azulenyl groups, anthryl groups, triphenylenyl groups, chrysenyl groups, fluorenylidene phenyl groups, and 5H-dibenzo[a,d] cycloheptenylidene phenyl groups), non-condensed polycyclic ring groups (e.g., biphenylyl groups, and terphenylyl groups), and groups having the following formula.

【Formula 6】



wherein W represents $-O-$, $-S-$, $-SO-$, $-SO_2-$, $-CO-$ and a group having one of the following formulae.



wherein c is an integer of from 1 to 12, d is an integer of from 1 to 3, e is an integer of from 1 to 3, and f is an integer of from 1 to 3.

[0129]

Specific examples of the heterocyclic ring groups include thienyl groups, benzothienyl groups, furyl groups, benzofuryl groups, and carbazolyl groups.

[0130]

Specific examples of the arylene groups for use as Ar₁, Ar₂ and Ar₃ include divalent groups of the aryl groups mentioned above for use in R₇ and R₈. The groups Ar₁, Ar₂ and Ar₃ may be the same as or different from the others.

[0131]

The above-mentioned aryl groups can have a substituent. The substituents described below are examples of R₁₀₆, R₁₀₇ and R₁₀₈.

[0132]

(1) Halogen atoms, trifluoromethyl groups, cyano groups and nitro groups.

[0133]

(2) alkyl groups such as linear or branched alkyl groups having from 1 to 12 carbon atoms, preferably from 1 to 8 carbon atoms

and more preferably from 1 to 4 carbon atoms. These alkyl groups can be substituted with a halogen atom, a hydroxyl group or a cyano group, an alkoxy group having from 1 to 4 carbon atoms, a phenyl group, or a phenyl group which is optionally substituted with an alkyl group having from 1 to 4 carbon atoms or an alkoxy group having from 1 to 4 carbon atoms.

Specific examples of the alkyl groups include methyl groups, ethyl groups, n-propyl groups, i-propyl groups, t-butyl groups, s-butyl groups, n-butyl groups, i-butyl groups, trifluoromethyl groups, 2-hydroxyethyl groups, 2-cyanoethyl groups, 2-ethoxyethyl groups, 2-methoxyethyl groups, benzyl groups, 4-chlorobenzyl groups, 4-methylbenzyl groups, 4-methoxybenzyl groups, 4-phenylbenzyl groups, etc.

[0134]

(3) Alkoxy groups (-OR₁₀₉). Specific examples of the group R₁₀₉ include the alkyl groups defined above in numbered paragraph (2) above. Specific examples of the alkoxy groups include methoxy groups, ethoxy groups, n-propoxy groups, i-propoxy groups, t-butoxy groups, n-butoxy groups, i-butoxy groups, 2-hydroxyethoxy groups, 2-cyanoethoxy groups, benzyloxy groups, 4-methylbenzyloxy groups, trifluoromethoxy groups, etc.

[0135]

(4) Aryloxy groups. Specific examples of the aryl group of the aryloxy groups include phenyl groups, and naphthyl groups, which can have a substituent such as alkoxy groups having from 1 to 4 carbon atoms, alkyl groups having from 1 to 4 carbon atoms, and halogen atoms. Specific examples of the aryloxy groups include phenoxy groups, 1-naphthoxy groups, 2-naphthoxy groups, 4-methylphenoxy groups, 4-methoxyphenoxy groups, 4-chlorophenoxy groups, 6-methyl-2-naphthoxy groups, etc.

[0136]

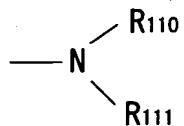
(5) Substituted mercapto groups and aryl mercapto groups.

Specific examples thereof include methylthio groups, ethylthio groups, phenylthio groups, p-methylphenylthio groups, etc.

[0137]

(6)

[Formula 7]



In the formula, the groups R_{110} and R_{111} are alkyl groups described above in numbered paragraph (2) above and aryl groups. Specific examples of the aryl groups include phenyl groups, biphenyl groups, and naphthyl groups. These groups can have a substituent such as alkoxy groups having from 1 to 4 carbon atoms, alkyl groups having from 1 to 4 carbon atoms, and halogen atoms. In addition, the nitrogen atom can share bond connectivity with a carbon atom in the aryl groups to form a ring.

Specific examples of the substituted amino groups include diethylamino groups, N-methyl-N-phenylamino groups, N,N-diphenylamino groups, N,N-di(p-tolyl)amino groups, dibenzylamino groups, piperidino groups, morphorino groups, julolidyl groups, etc.

[0138]

(7) Alkylenedioxy groups and alkylenedithio groups such as methylenedioxy groups and methylenedithio groups.

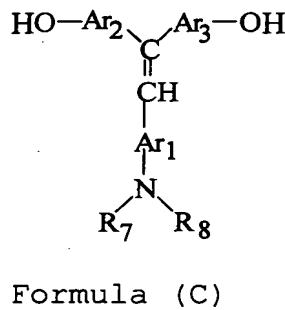
[0139]

The group X can be incorporated in the main chain of the polymers by polymerizing a diol compound having a triaryl amino group having the below-mentioned formula (C) together with a diol compound having the below-mentioned formula (B) using a method such as phosgene methods and ester exchange methods. In this case, the resultant polycarbonate resins are random or block copolymers. Alternatively, the group X can also be incorporated

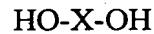
in the main chain by polymerizing the diol compound having formula (C) together with a bischloroformate which can be derived from the diol compound having formula (B). In this case, the resultant polymers are alternating copolymers.

【0140】

【Formula 8】



Formula (C)



Formula (B)

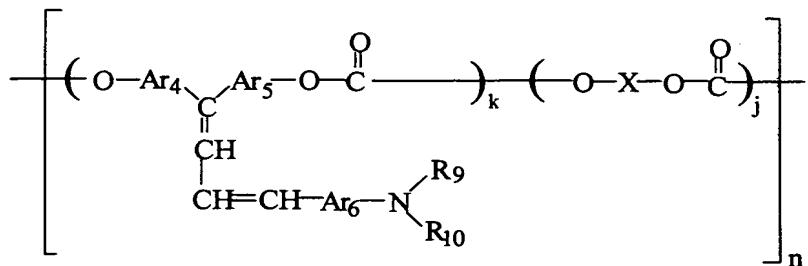
【0141】

Specific examples of the diol compounds (B) are mentioned above in formula 1.

[0142]

【Formula 9】

(formula 3)



(0143)

In the formula, R_9 and R_{10} represent a substituted or unsubstituted aryl group; Ar_4 , Ar_5 and Ar_6 independently represent an arylene group; and X , k , j and n are defined above in formula 1.

[0144]

[Specific examples of polymers having formula 3]

R_9 and R_{10} represent a substituted or unsubstituted aryl group. Specific examples thereof include the following. The groups R_9 and R_{10} may be the same as or different from the other.

【0145】

Specific examples of the aromatic hydrocarbon groups for use as the groups R_9 and R_{10} include a phenyl group, condensed ring groups (e.g., naphthyl groups, pyrenyl groups, 2-fluorenyl groups, 9,9-dimethyl-2-fluorenyl groups, azulenyl groups, anthryl groups, triphenylenyl groups, chrysenyl groups, fluorenylidene phenyl groups, and 5H-dibenzo[a,d] cycloheptenylidene phenyl groups), and non-condensed polycyclic ring groups (e.g., biphenylyl groups, and terphenylyl groups).

【0146】

Specific examples of the heterocyclic ring groups for use as the groups R_9 and R_{10} include thiienyl groups, benzothienyl groups, furyl groups, benzofuryl groups, and carbazolyl groups.

【0147】

As the arylene groups for use in Ar_4 , Ar_5 and Ar_6 , divalent groups of the aryl groups mentioned above for use in R_9 and R_{10} can be used. The above-mentioned aryl groups and arylene groups can have a substituent. Specific examples of the substituent include the following groups.

【0148】

(1) Halogen atoms, trifluoromethyl groups, cyano groups and nitro groups.

【0149】

(2) Alkyl groups such as linear or branched alkyl groups having from 1 to 12 carbon atoms, preferably from 1 to 8 carbon atoms and more preferably from 1 to 4 carbon atoms. These alkyl groups can be substituted with a halogen atom, a hydroxyl group or a

cyano group, an alkoxy group having from 1 to 4 carbon atoms, a phenyl group, or a phenyl group which is optionally substituted with an alkyl group having from 1 to 4 carbon atoms or an alkoxy group having from 1 to 4 carbon atoms.

Specific examples of the alkyl groups include methyl groups, ethyl groups, n-propyl groups, i-propyl groups, t-butyl groups, s-butyl groups, n-butyl groups, i-butyl groups, trifluoromethyl groups, 2-hydroxyethyl groups, 2-cyanoethyl groups, 2-ethoxyethyl groups, 2-methoxyethyl groups, benzyl groups, 4-chlorobenzyl groups, 4-methylbenzyl groups, 4-methoxybenzyl groups, 4-phenylbenzyl groups, etc.

[0150]

(3) Alkoxy groups (-OR₁₁₂). Specific examples of the group R₁₁₂ include the alkyl groups defined in numbered paragraph (2) above. Specific examples of the alkoxy groups include methoxy groups, ethoxy groups, n-propoxy groups, i-propoxy groups, t-butoxy groups, n-butoxy groups, i-butoxy groups, 2-hydroxyethoxy groups, 2-cyanoethoxy groups, benzyloxy groups, 4-methylbenzyloxy groups, trifluoromethoxy groups, etc.

[0151]

(4) Aryloxy groups. Specific examples of the aryl group of the aryloxy groups include phenyl groups, and naphthyl groups, which can have a substituent such as alkoxy groups having from 1 to 4 carbon atoms, alkyl groups having from 1 to 4 carbon atoms, and halogen atoms. Specific examples of the aryloxy groups include phenoxy groups, 1-naphthoxy groups, 2-naphthoxy groups, 4-methylphenoxy groups, 4-methoxyphenoxy groups, 4-chlorophenoxy groups, 6-methyl-2-naphthoxy groups, etc.

[0152]

(5) Substituted mercapto groups and aryl mercapto groups. Specific examples thereof include methylthio groups, ethylthio groups, phenylthio groups, p-methylphenylthio groups, etc.

【0153】

(6) Amino groups substituted with an alkyl group. Specific examples of the alkyl groups are mentioned above in numbered paragraph (2) above. Specific examples of the substituted amino groups include dimethylamino groups, diethylamino groups, N-methyl-N-propylamino groups, N,N-dibenzylamino groups, etc.

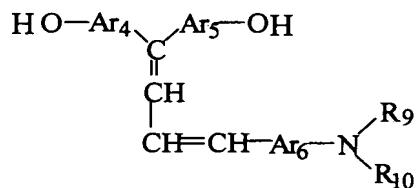
【0154】

(7) Acyl groups. Specific examples of the acyl groups include acetyl groups, propionyl groups, butylyl groups, malonyl groups, benzoyl groups, etc.

【0155】

The group X can be incorporated in the main chain of the polymers by polymerizing a diol compound having a triarylamino group having the below-mentioned formula (D) together with a diol compound having the below-mentioned formula (B) using a method such as phosgene methods and ester exchange methods. In this case, the resultant polycarbonate resins are random or block copolymers. Alternatively, the group X can also be incorporated in the main chain by polymerizing the diol compound having formula (D) together with bischloroformate which can be derived from the diol compound having formula (B). In this case, the resultant polymers are alternating copolymers.

【Formula 10】



Formula (D)



Formula (B)

【0156】

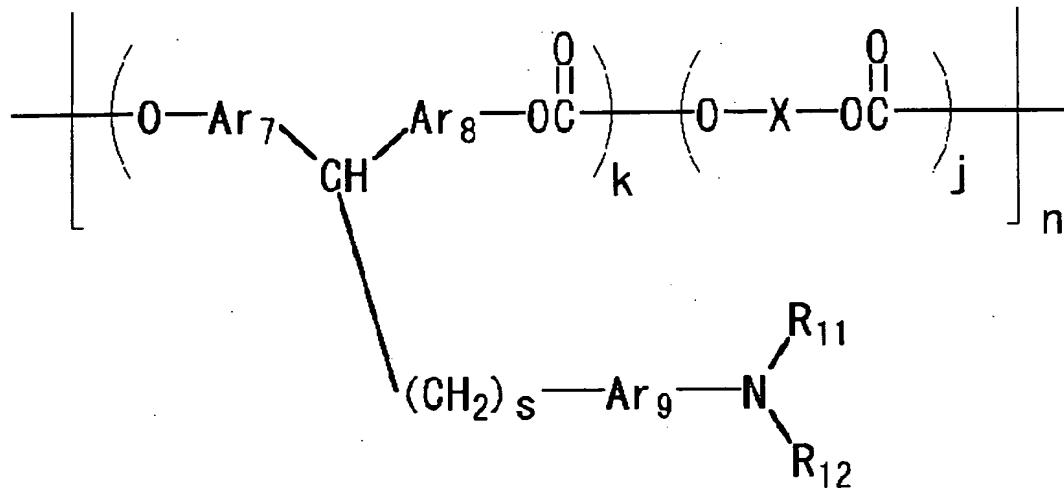
Specific examples of the diol compounds having formula (B) include the compounds mentioned above for use in the compounds

having formula 1.

[0157]

[Formula 11]

(Polymers having formula 4)



[0158]

In the formula, R_{11} and R_{12} represent a substituted or unsubstituted aryl group; Ar_7 , Ar_8 and Ar_9 independently represent an arylene group; s is an integer of from 1 to 5; and X , k , j and n are defined above in formula 1.

[0159]

[Specific examples of polymers having formula 4]

R_{11} and R_{12} represent a substituted or unsubstituted aryl group. Specific examples thereof include the following. The groups R_{11} and R_{12} may be the same as or different from the other.

Specific examples of the aromatic hydrocarbon groups for use as the groups R_{11} and R_{12} include phenyl groups, condensed ring groups (e.g., naphthyl groups, pyrenyl groups, 2-fluorenyl groups, 9,9-dimethyl-2-fluorenyl groups, azulenyl groups, anthryl groups, triphenylenyl groups, chrysenyl groups, fluorenylidene phenyl groups, and

5H-dibenzo[a,d] cycloheptenylidenephanyl groups), and non-condensed polycyclic ring groups (e.g., biphenylyl groups, and terphenylyl groups).

Specific examples of the heterocyclic ring groups include thiienyl groups, benzothienyl groups, furyl groups, benzofuryl groups, and carbazolyl groups.

【0160】

As the arylene groups for use in Ar₇, Ar₈ and Ar₉, divalent groups of the aryl groups mentioned above for use in R₁₁ and R₁₂ can be used. The groups Ar₇, Ar₈ and Ar₉ may be the same as or different from the others.

【0161】

The above-mentioned aryl groups and arylene groups can have a substituent. Specific examples of the substituent include the following groups.

【0162】

(1) Halogen atoms, trifluoromethyl groups, cyano groups and nitro groups.

【0163】

(2) Alkyl groups such as linear or branched alkyl groups having from 1 to 12 carbon atoms, preferably from 1 to 8 carbon atoms and more preferably from 1 to 4 carbon atoms. These alkyl groups can be substituted with a halogen atom, a hydroxyl group or a cyano group, an alkoxy group having from 1 to 4 carbon atoms, a phenyl group, or a phenyl group which is optionally substituted with an alkyl group having from 1 to 4 carbon atoms or an alkoxy group having from 1 to 4 carbon atoms.

Specific examples of the alkyl groups include methyl groups, ethyl groups, n-propyl groups, i-propyl groups, t-butyl groups, s-butyl groups, n-butyl groups, i-butyl groups, trifluoromethyl groups, 2-hydroxyethyl groups, 2-cyanoethyl groups, 2-ethoxyethyl groups, 2-methoxyethyl groups, benzyl groups,

4-chlorobenzyl groups, 4-methylbenzyl groups, 4-methoxybenzyl groups, 4-phenylbenzyl groups, etc.

[0164]

(3) Alkoxy groups ($-OR_{113}$). Specific examples of the group R_{113} include the alkyl groups defined in numbered paragraph (2) above. Specific examples of the alkoxy groups include methoxy groups, ethoxy groups, n-propoxy groups, i-propoxy groups, t-butoxy groups, n-butoxy groups, i-butoxy groups, 2-hydroxyethoxy groups, 2-cyanoethoxy groups, benzyloxy groups, 4-methylbenzyloxy groups, trifluoromethoxy groups, etc.

[0165]

(4) Aryloxy groups. Specific examples of the aryl group of the aryloxy groups include phenyl groups, and naphthyl groups, which can have a substituent such as alkoxy groups having from 1 to 4 carbon atoms, alkyl groups having from 1 to 4 carbon atoms, and halogen atoms. Specific examples of the aryloxy groups include phenoxy groups, 1-naphthyloxy groups, 2-naphthyloxy groups, 4-methylphenoxy groups, 4-methoxyphenoxy groups, 4-chlorophenoxy groups, 6-methyl-2-naphthyloxy groups, etc.

[0166]

(5) Substituted mercapto groups and aryl mercapto groups. Specific examples thereof include methylthio groups, ethylthio groups, phenylthio groups, p-methylphenylthio groups, etc.

[0167]

(6) Amino groups substituted with an alkyl group. Specific examples of the alkyl groups are mentioned above in numbered paragraph (2) above. Specific examples of the substituted amino groups include dimethylamino groups, diethylamino groups, N-methyl-N-propylamino groups, N,N-dibenzylamino groups, etc.

[0168]

(7) Acyl groups. Specific examples of the acyl groups include acetyl groups, propionyl groups, butylyl groups, malonyl groups,

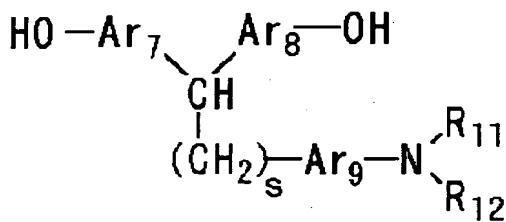
benzoyl groups, etc.

【0169】

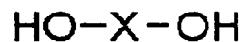
The group X can be incorporated in the main chain of the polymers by polymerizing a diol compound having a triarylarnino group having the below-mentioned formula (E) together with a diol compound having the below-mentioned formula (B) using a method such as phosgene methods and ester exchange methods. In this case, the resultant polycarbonate resins are random or block copolymers. Alternatively, the group X can also be incorporated in the main chain by polymerizing the diol compound having formula (E) together with bischloroformate which can be derived from the diol compound having formula (B). In this case, the resultant polymers are alternating copolymers.

【0170】

【Formula 12】



Formula (E)

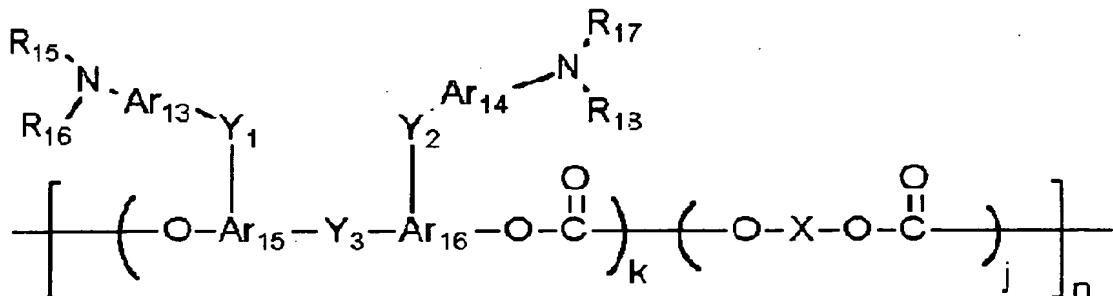


Formula (B)

【0171】

【Formula 13】

(formula 5)



【0172】

In the formula, R_{15} , R_{16} , R_{17} and R_{18} represent a substituted or unsubstituted aryl group; Ar_{13} , Ar_{14} , Ar_{15} and Ar_{16} independently represent an arylene group; Y_1 , Y_2 and Y_3 independently represent a single bond, a substituted or unsubstituted alkylene group, a substituted or unsubstituted cycloalkylene group, a substituted or unsubstituted alkyleneether group, an oxygen atom, a sulfur atom, or a vinylene group; and X , k , j and n are defined above in formula 1.

【0173】

[Specific examples of polymers having formula 5]

R_{15} , R_{16} , R_{17} and R_{18} represent a substituted or unsubstituted aryl group. Specific examples thereof include the following. The groups R_{15} , R_{16} , R_{17} and R_{18} may be the same as or different from the others.

【0174】

Specific examples of the aromatic hydrocarbon groups include phenyl groups, condensed ring groups (e.g., naphthyl groups, pyrenyl groups, 2-fluorenyl groups, 9,9-dimethyl-2-fluorenyl groups, azulenyl groups, anthryl groups, triphenylenyl groups, chrysenyl groups, fluorenylidene phenyl groups, and 5H-dibenzo[a,d] cycloheptenylidene phenyl groups), and non-condensed polycyclic ring groups (e.g., biphenylyl groups, and terphenylyl groups).

Specific examples of the heterocyclic ring groups include thienyl groups, benzothienyl groups, furyl groups, benzofuryl groups, and carbazolyl groups.

【0175】

As the arylene groups for use in the groups Ar_{13} , Ar_{14} , Ar_{15} and Ar_{16} , divalent groups of the aryl groups mentioned above for use in the groups R_{15} to R_{18} can be used.

【0176】

The above-mentioned aryl groups and arylene groups can have a substituent. Specific examples of the substituent include the following groups.

【0177】

(1) Halogen atoms, trifluoromethyl groups, cyano groups and nitro groups.

【0178】

(2) Alkyl groups such as linear or branched alkyl groups having from 1 to 12 carbon atoms, preferably from 1 to 8 carbon atoms and more preferably from 1 to 4 carbon atoms. These alkyl groups can be substituted with a halogen atom, a hydroxyl group or a cyano group, an alkoxy group having from 1 to 4 carbon atoms, a phenyl group, or a phenyl group which is optionally substituted with an alkyl group having from 1 to 4 carbon atoms or an alkoxy group having from 1 to 4 carbon atoms.

Specific examples of the alkyl groups include methyl groups, ethyl groups, n-propyl groups, i-propyl groups, t-butyl groups, s-butyl groups, n-butyl groups, i-butyl groups, trifluoromethyl groups, 2-hydroxyethyl groups, 2-cyanoethyl groups, 2-ethoxyethyl groups, 2-methoxyethyl groups, benzyl groups, 4-chlorobenzyl groups, 4-methylbenzyl groups, 4-methoxybenzyl groups, 4-phenylbenzyl groups, etc.

【0179】

(3) Alkoxy groups (-OR₁₁₅). Specific examples of the group R₁₁₅ include the alkyl groups defined in numbered paragraph (2) above. Specific examples of the alkoxy groups include methoxy groups, ethoxy groups, n-propoxy groups, i-propoxy groups, t-butoxy groups, n-butoxy groups, i-butoxy groups, 2-hydroxyethoxy groups, 2-cyanoethoxy groups, benzyloxy groups, 4-methylbenzyloxy groups, trifluoromethoxy groups, etc.

【0180】

(4) Aryloxy groups. Specific examples of the aryl group of the aryloxy groups include phenyl groups, and naphthyl groups, which can have a substituent such as alkoxy groups having from 1 to 4 carbon atoms, alkyl groups having from 1 to 4 carbon atoms, and halogen atoms. Specific examples of the aryloxy groups include phenoxy groups, 1-naphthoxy groups, 2-naphthoxy groups, 4-methylphenoxy groups, 4-methoxyphenoxy groups, 4-chlorophenoxy groups, 6-methyl-2-naphthoxy groups, etc.

[0181]

Y_1 , Y_2 and Y_3 independently represent a single bonding, a substituted or unsubstituted alkylene group, a substituted or unsubstituted cycloalkylene group, a substituted or unsubstituted alkylene ether group, an oxygen atom, a sulfur atom, or a vinylene group.

[0182]

As the alkylene group, divalent groups derived from the alkyl groups mentioned above in numbered paragraph (2) above can be used. Specific examples of the alkylene groups include methylene groups, ethylene groups, 1,3-propylene groups, 1,4-butylene groups, 2-methyl-1,3-propylene groups, difluoromethylene groups, hydroxyethylene groups, cyanoethylene groups, methoxyethylene groups, phenylmethylene groups, 4-methylphenylmethlene groups, 2,2-propylene groups, 2,2-butylene groups, diphenylmethlene groups, etc.

[0183]

Specific examples of the cycloalkylene groups include 1,1-cyclopentylene groups, 1,1-cyclooctylene groups, etc.

[0184]

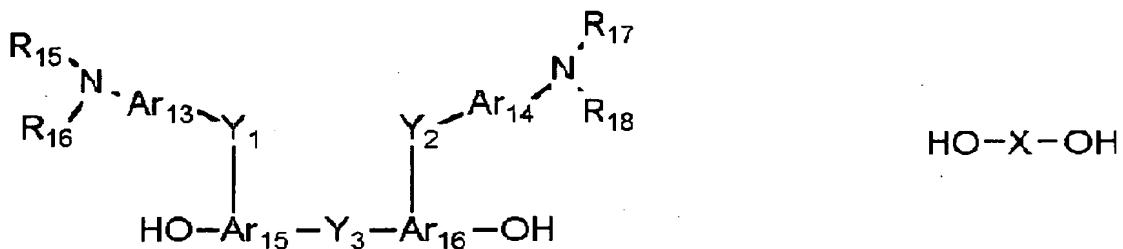
Specific examples of the alkylene ether groups include dimethylene ether groups, diethylene ether groups, ethylene methylene ether groups, bis(triethylene) ether groups, polytetramethylene ether groups, etc.

【0185】

The group X can be incorporated in the main chain of the polymers by polymerizing a diol compound having a triarylarnino group having the below-mentioned formula (G) together with a diol compound having the below-mentioned formula (B) using a method such as phosgene methods and ester exchange methods. In this case, the resultant polycarbonate resins are random or block copolymers. Alternatively, the group X can also be incorporated in the main chain by polymerizing the diol compound having formula (G) together with bischloroformate which can be derived from the diol compound having formula (B). In this case, the resultant polymers are alternating copolymers.

【0186】

【Formula 14】



Formula (G)

Formula (B)

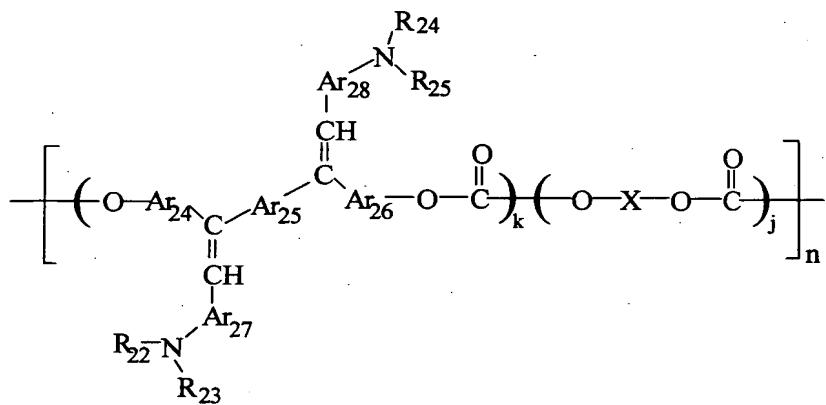
【0187】

Specific examples of the diol compounds having formula (B) include the compounds mentioned above for use in formula 1.

【0188】

【Formula 15】

(formula 6)



[0189]

In the formula, R_{22} , R_{23} , R_{24} and R_{25} represent a substituted or unsubstituted aryl group; Ar_{24} , Ar_{25} , Ar_{26} , Ar_{27} and Ar_{28} independently represent an arylene group; and X , k , j and n are defined above in formula 1.

[0190]

[Specific examples of polymers having formula 6]

R_{22} , R_{23} , R_{24} and R_{25} represent a substituted or unsubstituted aryl group. Specific examples thereof include the following. The groups R_{22} , R_{23} , R_{24} and R_{25} may the same as or different from the others.

[0191]

Specific examples of the aromatic hydrocarbon groups include phenyl groups, condensed ring groups (e.g., naphthyl groups, pyrenyl groups, 2-fluorenyl groups, 9,9-dimethyl-2-fluorenyl groups, azulenyl groups, anthryl groups, triphenyl groups, chrysenyl groups, fluorenylidene phenyl groups, and 5H-dibenzo[a,d] cycloheptenylidene phenyl groups), and non-condensed polycyclic ring groups (e.g., biphenylyl groups, and terphenylyl groups).

[0192]

Specific examples of the heterocyclic ring groups include

thienyl groups, benzothienyl groups, furyl groups, benzofuryl groups, and carbazolyl groups.

【0193】

As the arylene groups for use in the groups Ar_{24} , Ar_{25} , Ar_{26} and Ar_{27} , divalent groups of the aryl groups mentioned above for use in the groups R_{22} to R_{25} can be used.

【0194】

The above-mentioned aryl groups and arylene groups can have a substituent. Specific examples of the substituent include the following groups.

【0195】

(1) Halogen atoms, trifluoromethyl groups, cyano groups and nitro groups.

【0196】

(2) Alkyl groups such as linear or branched alkyl groups having from 1 to 12 carbon atoms, preferably from 1 to 8 carbon atoms and more preferably from 1 to 4 carbon atoms. These alkyl groups can be substituted with a halogen atom, a hydroxyl group or a cyano group, an alkoxy group having from 1 to 4 carbon atoms, a phenyl group, or a phenyl group which is optionally substituted with an alkyl group having from 1 to 4 carbon atoms or an alkoxy group having from 1 to 4 carbon atoms.

Specific examples of the alkyl groups include methyl groups, ethyl groups, n-propyl groups, i-propyl groups, t-butyl groups, s-butyl groups, n-butyl groups, i-butyl groups, trifluoromethyl groups, 2-hydroxyethyl groups, 2-cyanoethyl groups, 2-ethoxyethyl groups, 2-methoxyethyl groups; benzyl groups, 4-chlorobenzyl groups, 4-methylbenzyl groups, 4-methoxybenzyl groups, 4-phenylbenzyl groups, etc.

【0197】

(3) Alkoxy groups ($-OR_{118}$). Specific examples of the group R_{118} include the alkyl groups defined in numbered paragraph (2) above.

Specific examples of the alkoxy groups include methoxy groups, ethoxy groups, n-propoxy groups, i-propoxy groups, t-butoxy groups, n-butoxy groups, i-butoxy groups, 2-hydroxyethoxy groups, 2-cyanoethoxy groups, benzyloxy groups, 4-methylbenzyloxy groups, trifluoromethoxy groups, etc.

【0198】

(4) Aryloxy groups. Specific examples of the aryl group of the aryloxy groups include phenyl groups, and naphthyl groups, which can have a substituent such as alkoxy groups having from 1 to 4 carbon atoms, alkyl groups having from 1 to 4 carbon atoms, and halogen atoms. Specific examples of the aryloxy groups include phenoxy groups, 1-naphthyoxy groups, 2-naphthyoxy groups, 4-methylphenoxy groups, 4-methoxyphenoxy groups, 4-chlorophenoxy groups, 6-methyl-2-naphthyoxy groups, etc.

【0199】

(5) Substituted mercapto groups and aryl mercapto groups. Specific examples thereof include methylthio groups, ethylthio groups, phenylthio groups, p-methylphenylthio groups, etc.

【0200】

(6) Amino groups substituted with an alkyl group. Specific examples of the alkyl groups are mentioned above in numbered paragraph (2). Specific examples of the substituted amino groups include dimethylamino groups, diethylamino groups, N-methyl-N-propylamino groups, N,N-dibenzylamino groups, etc.

【0201】

(7) Acyl groups. Specific examples of the acyl groups include acetyl groups, propionyl groups, butylyl groups, malonyl groups, benzoyl groups, etc.

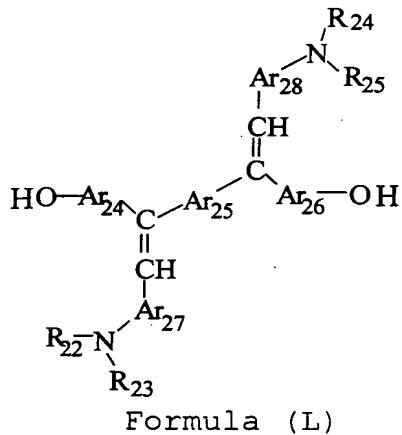
【0202】

The group X can be incorporated in the main chain of the polymers by polymerizing a diol compound having a triarylamino group having the below-mentioned formula (L) together with a

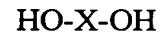
diol compound having the below-mentioned formula (B) using a method such as phosgene methods and ester exchange methods. In this case, the resultant polycarbonate resins are random or block copolymers. Alternatively, the group X can also be incorporated in the main chain by polymerizing the diol compound having formula (L) together with bischloroformate which can be derived from the diol compound having formula (B). In this case, the resultant polymers are alternating copolymers.

【0203】

【Formula 16】



Formula (L)



Formula (B)

【0204】

Specific examples of the diol compounds having formula (B) include the compounds mentioned above for use in formula 1.

【0205】

Specific examples of the polycarbonate having a triaryl amine structure in its side chains include compounds disclosed in published unexamined Japanese patent applications Nos. 6-234838, 6-234839, 6-295077, 7-325409, 9-297419, 9-80783, 9-80784, 9-80772, 9-265201, etc.

【0206】

In the charge transport polymers, repeat units having an electrically inactive structure are obtained from monomers which

do not have a photoconductive property that compounds having triaryl amine structure have. Specific examples of such repeat units include the repeat units mentioned above in formula (B).

The above-mentioned charge transport polymers can be used alone or in combination.

【0207】

Suitable methods for forming the charge generation layer include thin film forming methods in a vacuum, and casting methods.

Specific examples of such thin film forming methods in a vacuum include vacuum evaporation methods, glow discharge decomposition methods, ion plating methods, sputtering methods, reaction sputtering methods, CVD (chemical vapor deposition) methods, etc. A layer of the above-mentioned inorganic and organic materials can be formed by one of these methods.

The casting methods for forming the charge generation layer typically include preparing a coating liquid by mixing one or more inorganic or organic charge generation materials mentioned above with a solvent such as tetrahydrofuran, cyclohexanone, dioxane, dichloroethane, butanone, etc., optionally together with a binder resin and an additive, and then dispersing the materials with a ball mill, an attritor, a sand mill, etc., to prepare a dispersion; and coating the dispersion, which is diluted if necessary, by a method such as dip coating, spray coating, bead coating and ring coating.

【0208】

The thickness of the CGL is preferably from about 0.01 to about 5 μm , and more preferably from about 0.05 to about 2 μm .

【0209】

Next the charge transport layer 26 will be explained. The charge transport layer is typically prepared by

preparing a coating liquid in which a mixture or a copolymer of a charge transport material and a binder resin is dissolved or dispersed in a solvent, and then coating the coating liquid followed by drying.

【0210】

Specific examples of the polymers for use as the binder resin of the charge transport layer include thermoplastic resins and thermosetting resins such as polystyrene, styrene / acrylonitrile copolymers, styrene / butadiene copolymers, styrene / maleic anhydride copolymers, polyester, polyvinyl chloride, vinyl chloride / vinyl acetate copolymers, polyvinyl acetate, polyvinylidene chloride, polyarylate, polycarbonate, cellulose acetate resins, ethyl cellulose resins, polyvinyl butyral, polyvinyl formal, polyvinyl toluene, acrylic resins, silicone resins, fluorine-containing resins, epoxy resins, melamine resins, urethane resins, phenolic resins and alkyd resins, but are not limited thereto.

【0211】

These polymer materials can be used alone or in combination. In addition, copolymers of the monomers of the polymer materials mentioned above can also be used. Further, copolymers of the monomers with a charge transport material can also be used.

When a protective layer is prepared by coating, the charge transport layer preferably includes a resin soluble in the solvent of the protective layer coating liquid to be coated thereon, such as polystyrene, polyarylate, polycarbonate and phenolic resins, to make the interface between the protective layer and the charge transport layer unclear.

【0212】

When an electrically inactive polymer is used in order to impart good stability to withstand environmental conditions to the resultant photoreceptor, resins such as polyester,

polycarbonate, acrylic resins, polystyrene, polyvinylidene chloride, polyethylene, polypropylene, fluorine-containing resins, polyacrylonitrile, acrylonitrile / styrene / butadiene copolymers, acrylonitrile / styrene copolymers and ethylene / vinyl acetate copolymers are preferably used.

【0213】

In this regard, electrically inactive charge transport polymer materials mean polymers which do not have a structure having a photoconductive property, such as the triarylamine structure.

Repeat units having an electrically inactive structure can be obtained from monomers which do not have a photoconductive property that compounds having a triaryl amine structure have. Specific examples of repeat units include those mentioned above in formula (B).

【0214】

When these resins are used as an additive together with a binder resin, the content thereof is preferably not greater than 50 % by weight in view of photosensitivity of the resultant photoreceptor.

【0215】

Specific examples of the charge transport materials for use in the charge transport layer include low molecular weight electron transport materials, low molecular weight positive hole transport materials, and charge transport polymers.

When a low molecular weight charge transport material is used, the content thereof is preferably from 40 to 200 parts by weight, and preferably from 70 to 150 parts by weight, per 100 parts by weight of the resin components included therein. When a charge transport polymer is used, the content thereof is preferably from 0 to 500 parts by weight, and preferably from 0 to 150 parts by weight, per 100 parts by weight of the charge

transport components included therein.

【0216】

When two or more kinds of charge transport materials are included in the charge transport layer, the difference in ionization potential between the two or more kinds of charge transport materials is as small as possible. Specifically, the difference is preferably not greater than 0.15 eV. In this case, it is prevented that one of the charge transport materials serves as a trap of the other charge transport materials.

【0217】

Forming a protective layer is disadvantageous to the photosensitivity of the photoreceptor. In order to avoid deterioration of photosensitivity, it is preferable to enhance the charge mobility of the charge transport layer, particularly at a low electric field. Specifically, the charge mobility of the charge transport layer or the protective layer mentioned below is preferably not less than $1.2 \times 10^{-5} \text{ cm}^2/\text{V} \cdot \text{sec}$ at an electric field strength of $4 \times 10^5 \text{ V/cm}$. In addition, the dependence (β) of the charge mobility on the electric field strength, which is defined below, is preferably not greater than 1.6×10^{-3} .

【0218】

The dependence (β) can be determined as follows. The charge mobility of a charge transport layer is measured while the electric field strength is changed. As illustrated in FIG. 11, the data are plotted in a semilogarithmic paper while the charge mobility is plotted on the vertical axis in units of $\text{cm}^2/\text{V} \cdot \text{sec}$ and the square root of the electric field is plotted on the horizontal axis in units of $\text{V}^{1/2}/\text{cm}^{1/2}$, to obtain an approximation line. A specific example is illustrated in FIG. 11. As the slope of the line becomes sharper, the dependence of the mobility on the electric field strength is considered to be stronger.

In order to quantitatively express the dependence, the following equation [1] is used.

$$\beta = \log \mu/E^{1/2} \quad [1] .$$

【0219】

It is said that when a charge transport layer has a large β , the charge mobility of the charge transport layer largely changes depending on the electric field strength.

A charge transport layer with large β typically has a low charge mobility at a low electric field. Therefore, when such a charge transport layer is used for a photoreceptor, the photoreceptor has disadvantages such that residual potential increases; and when the photoreceptor is used while the potential of the charged photoreceptor is decreased, a case where the photoreceptor has poor response arises.

【0220】

In order to impart high photosensitivity to a photoreceptor, the content of charge transport components in the charge transport layer is preferably not less than 70 parts by weight per 100 parts by weight of the resin components in the charge transport layer.

【0221】

Suitable solvents for use in preparing a charge transport layer coating liquid include ketones such as methyl ethyl ketone, acetone, methyl isobutyl ketone, and cyclohexanone; ethers such as dioxane, tetrahydrofuran, and ethyl cellosolve; aromatic solvents such as toluene, and xylene; halogen-containing solvents such as chlorobenzene, and dichloromethane; esters such as ethyl acetate and butyl acetate; etc. These solvents can be used alone or in combination.

【0222】

The charge transport layer can include one or more additives such as low molecular weight compounds, e.g.,

antioxidants, plasticizers, lubricants and ultraviolet absorbents, and leveling agents, which are mentioned below, if desired. These additives are used alone or in combination. These additives are added in the charge transport layer in an amount of from 0.1 to 50 parts by weight, preferably from 0.1 to 20 parts by weight, per 100 parts by weight of the polymer components therein. The leveling agents are added in an amount of from 0.001 to 5 parts by weight per 100 parts by weight of the polymer components therein.

【0223】

Suitable coating methods for use in coating the charge transport layer coating liquid included dip coating methods, spray coating methods, ring coating methods, roll coating methods, gravure coating methods, nozzle coating methods, screenprinting methods, etc.

【0224】

The thickness of the charge transport layer is generally from 15 to 40 μm , and preferably from 15 to 30 μm . When it is desired to form images having good resolution, the thickness of the charge transport layer is preferably not greater than 25 μm .

【0225】

Then the mixture type photosensitive layer 22 will be explained.

The mixture type photosensitive layer can be prepared by coating a coating liquid in which constituents of the photosensitive layer are dissolved or dispersed in a proper solvent, and then drying the coated liquid. Suitable coating methods include the coating methods mentioned above for use in preparing the charge transport layer. In addition, suitable binder resins, charge generation materials, and charge transport materials for use in the mixture type photosensitive layer

include those mentioned above.

【0226】

The mixture type photosensitive layer can include additives such as low molecular weight compounds, e.g., antioxidants, plasticizers, lubricants, and ultraviolet absorbents, and leveling agents. These additives can be used alone or in combination.

The low molecular weight compounds are added in the charge transport layer in an amount of from 0.1 to 100 parts by weight, preferably from 0.1 to 30 parts by weight, per 100 parts by weight of the polymer components therein. The leveling agents are added in an amount of from 0.001 to 5 parts by weight per 100 parts by weight of the polymer components therein.

【0227】

The thickness of the mixture type photosensitive layer is generally from 5 to 50 μm , and preferably from 10 to 35 μm . When it is desired to form images having good resolution, the thickness of the mixture type photosensitive layer is preferably from 10 to 28 μm .

【0228】

Then the protective layer 23 will be explained.

In the present invention, the protective layer is formed on the photosensitive layer as an outermost layer to improve the abrasion resistance and slidability of the photoreceptor.

The protective layer can be formed only by a resin or a mixture of a resin and a filler or a slidability improving agent. Specific examples of the resins for use in the protective layer include binder resins mentioned above for use in the charge generation layer and the charge transport polymers mentioned above.

When a thermoplastic resin is used for the protective layer, it is preferable that the protective layer is formed in such

a manner that no interface is formed between the protective layer and the underlying photosensitive layer (or charge transport layer). Therefore, it is preferable to use a resin, which can be mixed with the resin in the photosensitive layer, for the protective layer (for example, the same resin as that used for the photosensitive layer (or charge transport layer) is used for the protective layer).

【0229】

When the protective layer is formed, the following relationship is preferably satisfied:

$$1.3 < W1/W2 < 1.9,$$

wherein W1 represents the weight of the protective layer, which is measured after coating the protective layer coating liquid and allowing the coated liquid to settle for 1 hour under conditions of 25 ± 3 °C and 53 ± 5 %RH; and W2 represents the weight of the protective layer, which is measured after coating the protective layer coating liquid and drying the coated liquid upon application of heat thereto. In this case, the charge transport material included in the photosensitive layer properly diffuses into the protective layer and thereby the charges induced in the photosensitive layer by imagewise light can be fully injected into the protective layer.

【0230】

When a crosslinking resin is used for the protective layer, it is preferable that a charge transporting group is incorporated in the crosslinking resin or a charge transport polymer is included in the protective layer, so that charge carriers induced by imagewise light pass through the protective layer. It is also possible that a low molecular weight charge transport material is included in the protective layer in combination with a crosslinking resin if the low molecular weight charge transport material is mixable with the crosslinking resin. However, in

this case a bleeding problem often occurs such that the low molecular weight charge transport material is precipitated on the surface of the protective layer by bleeding from the protective layer without being fixed therein.

【0231】

Specific examples of the filler for use in the protective layer include titanium oxide, silica, silicone rubbers, alumina, zirconium oxide, antimony oxide, magnesium oxide, silicon nitride, boron nitride, calcium oxide, calcium carbonate, barium sulfate, etc. In particular, silica and α -alumina are preferable because of having good charge properties and good durability improving effect.

These fillers can be subjected to a surface treatment to improve the dispersibility thereof in the coating liquid and the coated layer.

【0232】

In order to improve the slidability of the photoreceptor, for example, slidability improving agents such as particulate polyolefins (disclosed in published unexamined Japanese patent application No. 11-212284), fluorine-containing oils (disclosed in published unexamined Japanese patent application No. 11-258843), silicone resin powders (disclosed in published unexamined Japanese patent application No. 11-265082), silicone oils (disclosed in unexamined Japanese patent application No. 11-271999), spherical particles of vinyl type thermoplastic polymers or condensed thermoplastic polymers (disclosed in published unexamined Japanese patent application No. 11-295911), and fluorine resin powders (disclosed in published unexamined Japanese patent application No. 11-305470) can also be used for the protective layer.

【0233】

The protective layer coating liquid is typically prepared

by mixing a filler or a slidability improving agent with a binder resin in a proper solvent. If necessary, the filler or slidability improving agent is subjected to a dispersion treatment (or a dissociating treatment).

【0234】

In order to reduce the potential of lighted portions of the photoreceptor, a resistivity decreasing agent can be contained in the protective layer. Specific examples of the resistivity decreasing agent include polyhydric alcohols partially esterified with fatty acids (e.g., mono esters of sorbitan with fatty acids, esters of pentaerythritol with fatty acids, etc.), ethylene oxide adducts of aliphatic alcohols, ethylene oxide adducts of fatty acids, ethylene oxide adducts of alkyl phenols, ethylene oxides adducts of polyhydric alcohols partially esterified with fatty acids, carboxylic acid derivatives, etc.

【0235】

Suitable solvents for use in preparing the protective layer coating liquid include the ketones, ethers, aromatic compounds, halogen-containing compounds, esters, etc. mentioned above for use in preparing the charge transport layer.

The dispersing treatment and the dissociating treatment for the fillers and slidability improving agents can be performed using ball mills, vibration mills, sand mills, KD mills, three-roll mills, pressure homogenizers, liquid-colliding-type dispersion machines, pressure jet mills, supersonic dispersion machines, etc.

【0236】

The content of the filler or the slidability improving agent in the protective layer is preferably from 5 to 70% by weight, and more preferably not lower than 10%. When the content is lower than 5% by weight, the protective layer has insufficient

properties. In contrast, when the content is higher than 70% by weight, a protective layer having a smooth surface cannot be formed. Therefore, it is preferable that the content is not higher than 70% by weight.

Suitable coating methods for use in forming the protective layer include the coating methods mentioned above for use in forming the charge transport layer. In particular, spray coating methods and ring coating methods are preferable because a protective layer having the desired properties can be stably produced.

【0237】

The thickness of the protective layer is from 0.5 to 15 μm , and preferably from 2 to 10 μm . When the thickness of the protective layer is less than 0.5 μm , the resultant photoreceptor has insufficient durability and slidability. In contrast, when the thickness is not less than 2 μm , the photoreceptor has as long life as that of other parts and devices of the image forming system.

【0238】

In general, the residual potential of a photoreceptor increases in proportion to square of the thickness of the protective layer thereof. Therefore, the thickness of the protective layer is preferably determined so that the transition time of the photoreceptor is shorter than the exposure-development interval in the image forming apparatus for which the photoreceptor is used. In this case, it is possible to prevent delayed carriers from staying in the photosensitive layer and protective layer, and thereby formation of residual images can be avoided.

However, since the photoreceptor of the present invention has a property such that the potential of a lighted portion of the photoreceptor changes at a rate of not greater than 700 V/sec

not earlier than 35 msec after the light irradiation in the light irradiation-development interval, this limitation is not necessary for the photoreceptor. Therefore, the protective layer can be thickened, and thereby the photoreceptor has long life. However, the protective layer is too thick, the manufacturing cost of the photoreceptor increases. Therefore, the upper limit of thickness is about 10 μm .

【0239】

If desired, the protective layer can include additives such as low molecular weight compounds, e.g., antioxidants, plasticizers, and ultraviolet absorbents, and leveling agents. The additives can be used alone or in combination.

【0240】

In the photoreceptor of the present invention, an undercoat layer 24 can be formed between the electroconductive substrate and the mixture-type photosensitive layer (or the charge generation layer) to improve adhesion between the substrate and the photosensitive layer; to prevent formation of moiré; to improve the coating property of the overlying layer; to reduce the residual potential; and to prevent injection of charges from the substrate into the photosensitive layer.

【0241】

The undercoat layer typically includes a resin as a main component. Since a photosensitive layer is typically formed on the undercoat layer by coating a liquid including an organic solvent, the resin in the undercoat layer preferably has good resistance to general organic solvents.

Specific examples of such resins include water-soluble resins such as polyvinyl alcohol resins, casein and polyacrylic acid sodium salts; alcohol soluble resins such as nylon copolymers and methoxymethylated nylon resins; and thermosetting resins capable of forming a three-dimensional

network such as polyurethane resins, melamine resins, alkyd-melamine resins, epoxy resins, etc.

The undercoat layer can include a fine powder of metal oxides such as titanium oxide, silica, alumina, zirconium oxide, tin oxide and indium oxide; metal sulfides; or metal nitrides.

【0242】

The undercoat layer can also be formed by coating a coating liquid using a proper solvent and a proper coating method, such as those mentioned above for use in preparing the photosensitive layer.

【0243】

In addition, metal oxide layers formed by a sol-gel method using a silane coupling agent, titanium coupling agent or a chromium coupling agent can also be used as the undercoat layer.

Further, a layer of aluminum oxide which is formed by an anodic oxidation method and a layer of an organic compound such as polyparaxylylene or an inorganic compound such as silica, tin oxide, titanium oxide, ITO or ceria, which is formed by a vacuum evaporation method, is also preferably used as the undercoat layer.

【0244】

The thickness of the undercoat layer is preferably 0.1 to 5 μm .

【0245】

In the photoreceptor of the present invention, one or more additives such as antioxidants, plasticizers, lubricants, ultraviolet absorbents, low molecular weight charge transport materials and leveling agents can be used in each of the layers of the photoreceptor to improve the gas barrier property of the outermost layer of the photoreceptor and the stability thereof to withstand environmental conditions. Specific examples of the compounds are as follows.

【0246】

Specific examples of the antioxidants for use in the layers of the photoreceptor include the following compounds (a) to (d), but are not limited thereto.

【0247】

(a) Phenol-based antioxidants

2,6-di-t-butyl-p-cresol, 2,4,6-tri-t-butylphenol, n-octadecyl-3-(4'-hydroxy-3',5'-di-t-butylphenol)propionate, styrenated phenol, 4-hydroxymethyl-2,6-di-t-butylphenol, 2,5-di-t-butylhydroquinone, cyclohexylphenol, butylhydroxyanisole, 2,2'-methylene-bis(4-ethyl-6-t-butylphenol), 4,4-i-propylidenebisphenol, 1,1-bis(4-hydroxyphenyl)cyclohexane, 4,4'-methylen-bis(2,6-di-t-butylphenol), 2,6-bis(2'-hydroxy-3'-t-butyl-5' methylbenzyl)-4-methylphenol, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 1,3,5-trismethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene, tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] methane, tris(3,5-di-t-butyl-4-hydroxyphenyl)isocyanate, tris[β -(3,5-di-t-butyl-4-hydroxyphenyl)propionyl-oxyethyl] isocyanate, 4,4'-thiobis(3-methyl-6-t-butylphenol), 2,2'-thiobis(4-methyl-6-t-butylphenol), 4,4'-thiobis(4-methyl-6-t-butylphenol), etc.

【0248】

(b) Amine-based antioxidants

Phenyl- α -naphthylamine, phenyl- β -naphthylamine, N,N'-diphenyl-p-phenylenediamine, N,N'-di- β -naphthyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-

p-phenylenediamine, N-phenylene-N' -i-propyl-
p-phenylenediamine, aldol- α -naphthylamine,
6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline, etc.

[0249]

(c) sulfur-based antioxidants

Thiobis(β -naphthol), thiobis(N-phenyl- β -naphthylamine), 2-mercaptopbenzothiazole, 2-mercaptopbenzoimidazole, dodecylmercaptan, tetramethylthiurammoniumsulfide, tetramethylthiuramdisulfide, nickel dibutylthiocarbamate, isopropylxanthate, dilaurylthiodipropionate, distearylthiodipropionate, etc.

[0250]

(d) Phosphorus-based antioxidants

Triphenylphosphite, diphenyldecylphosphite, phenylisodecylphosphite, tri(nonylphenyl)phosphite, 4,4'-butyldene-bis(3-methyl-6-t-butylphenyl)-ditridecylphosphite, distearyl-pentaerythritoldiphosphite, trilaurylthiophosphite, etc.

[0251]

Specific examples of the plasticizers for use in the layers of the photoreceptor include the following compounds (a) to (m), but are not limited thereto.

[0252]

(a) Phosphoric acid ester-based plasticizers

Triphenyl phosphate, tricresyl phosphate, trioctyl phosphate, octyldiphenyl phosphate, trichloroethyl phosphate, cresyldiphenyl phosphate, tributyl phosphate, tri-2-ethylhexyl phosphate, triphenyl phosphate, etc.

[0253]

(b) Phthalic acid ester-based plasticizers

Dimethyl phthalate, diethyl phthalate, diisobutyl phthalate, dibutyl phthalate, diheptyl phthalate,

di-2-ethylhexyl phthalate, diisooctyl phthalate, di-n-octyl phthalate, dinonyl phthalate, diisononyl phthalate, diisodecyl phthalate, diundecyl phthalate, ditridecyl phthalate, dicyclohexyl phthalate, butylbenzyl phthalate, butyllauryl phthalate, methyloleyl phthalate, octyldecyl phthalate, dibutyl fumarate, dioctyl fumarate, etc.

【0254】

(c) Aromatic carboxylic acid ester-based plasticizers

Trioctyl trimellitate, tri-n-octyl trimellitate, octyl oxybenzoate, etc.

【0255】

(d) Dibasic fatty acid ester-based plasticizers

Dibutyl adipate, di-n-hexyl adipate, di-2-ethylhexyl adipate, di-n-octyl adipate, n-octyl-n-decyl adipate, diisodecyl adipate, dialkyl adipate, dicapryl adipate, di-2-ethylhexyl azelate, dimethyl sebacate, diethyl sebacate, dibutyl sebacate, di-n-octyl sebacate, di-2-ethylhexyl sebacate, di-2-ethoxyethyl sebacate, dioctyl succinate, diisodecyl succinate, dioctyl tetrahydrophthalate, di-n-octyl tetrahydrophthalate, etc.

【0256】

(e) Fatty acid ester derivatives

Butyl oleate, glycerin monooleate, methyl acetylricinolate, pentaerythritol esters, dipentaerythritol hexaesters, triacetin, tributyrin, etc.

【0257】

(f) Oxyacid ester-based plasticizers

Methyl acetylricinolate, butyl acetylricinolate, butylphthalylbutyl glycolate, tributyl acetylcitrate, etc.

【0258】

(g) Epoxy-based plasticizers

Epoxydized soybean oil, epoxydized linseed oil, butyl

epoxystearate, decyl epoxystearate, octyl epoxystearate, benzyl epoxystearate, dioctylepoxyhexahydrophthalate, didecyl epoxyhexahydrophthalate, etc.

【0259】

(h) Dihydric alcohol ester-based plasticizers

Diethylene glycol dibenzoate, triethylene glycol di-2-ethylbutyrate, etc.

【0260】

(i) Chlorine-containing plasticizers

Chlorinated paraffin, chlorinated diphenyl, methyl esters of chlorinated fatty acids, methyl esters of methoxychlorinated fatty acids, etc.

【0261】

(j) Polyester plasticizers

Polypropylene adipate, polypropylene sebacate, polyesters, acetylated polyesters, etc.

【0262】

(k) Sulfonic acid derivatives

p-toluene sulfonamide, o-toluene sulfonamide, p-toluene sulfoneethylamide, o-toluene sulfoneethylamide, toluene sulfone-N-ethylamide, p-toluene sulfone-N-cyclohexylamide, etc.

【0263】

(l) Citric acid derivatives

Triethyl citrate, triethyl acetylcitrate, tributyl citrate, tributyl acetylcitrate, tri-2-ethylhexyl acetylcitrate, n-octyldecyl acetylcitrate, etc.

【0264】

(m) Others

Terphenyl, partially hydrated terphenyl, camphor, 2-nitro diphenyl, dinonyl naphthalene, methyl abietate, etc.

【0265】

Specific examples of the ultraviolet absorbing agents for use in each of the layers of the photoreceptor include the following compounds, but are not limited thereto.

【0266】

(a) Benzophenone compounds

2-hydroxybenzophenone, 2,4-dihydroxybenzophenone,
2,2',4-trihydroxybenzophenone,
2,2',4,4'-tetrahydroxybenzophenone,
2,2'-dihydroxy-4-methoxybenzophenone, etc.

【0267】

(b) Salicylate compounds

Phenyl salicylate,
2,4-di-t-butylphenyl-3,5-di-t-butyl-4-hydroxybenzoate, etc.

【0268】

(c) Benzotriazole compounds

(2'-hydroxyphenyl)benzotriazole,
(2'-hydroxy-5'-methylphenyl)benzotriazole,
(2'-hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole, etc.

【0269】

(d) Cyano acrylate compounds

Ethyl-2-cyano-3,3-diphenyl acrylate,
methyl-2-carbomethoxy-3-(paramethoxy) acrylate, etc.

【0270】

(e) Quenchers (metal complexes)

Nickel[2,2'-thiobis(4-t-octyl)phenolate]-n-butylamine,
nickeldibutylthiocarbamate,
cobaltdicyclohexylthiophosphate, etc.

【0271】

(f) HALS (hindered amines)

Bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate,
bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate,

1-[2-{ 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy} ethyl]-4-{ 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy} -2,2,6,6-tetramethylpyridine,
8-benzyl-7,7,9,9-tetramethyl-3-octyl-1,3,8-triazaspiro[4,5]undecane-2,4-dione,
4-benzyloxy-2,2,6,6-tetramethylpiperidine, etc.

【0272】

Specific examples of the low molecular weight charge transport materials for use in each of the layers include the charge transport materials mentioned above for use in the charge generation layer 25.

【0273】

【Examples】

Hereinafter the present invention will be explained in detail referring to examples.

At first, the measurement methods used for the present invention will be explained.

【0274】

(1) Measurements of transition time of photoreceptor

The apparatus for evaluating the properties of photoreceptors, which is described in published unexamined Japanese patent application No. 2000-275872, was used to determine change of potential of a lighted portion with time during the light irradiation-development interval (Ted), and the transition time.

The measuring conditions were as follows.

Linear speed of photoreceptor (mm/s): 160

Resolution in the sub-scanning direction (dpi): 400

Power of light on the image forming surface (mW): 0.30
(exposure: 0.40 μ J/cm²)

Discharger: operated

Charger: Charging conditions were controlled so that the

photoreceptor has a potential of -800 V.

The angle of the probe of the potential meter, which is located at the position of the developing device, was changed to change the interval (Ted) between the light irradiation and development.

【0275】

(2) Measurements of thickness of photosensitive layer

The thickness of the photoreceptor was measured at intervals of 1 cm in the longitudinal direction of the photoreceptor by a thicknessmeter, FISCHER SCOPE mms, manufactured by Fischer Instruments, which measures thickness utilizing eddy current, to determine the average thickness of the photoreceptor.

【0276】

(3) Measurements of charge mobility

The charge transport layer coating liquid was coated on a polyethylene terephthalate film having an aluminum layer deposited thereon, followed by drying, to form a charge transport layer having a thickness of 10 μ m. A gold electrode with a thickness of 200 \AA was formed on the charge transport layer by vapor deposition to prepare a sample cell.

The charge mobility was measured by a Time Of Flight method, which is as follows:

A negative voltage is applied to the gold electrode on the charge transport layer sandwiched by the gold electrode and the aluminum electrode which is grounded through a resistor. Nitrogen gas laser light irradiates the charge transport layer from the gold electrode side while recording change of the voltage generated at the resistor due to the photo-current flowing the resistor using a digital oscilloscope. Two tangent lines are drawn at the start and end of the thus obtained voltage curve, respectively, to determine the transit time (t) which is the

intersection of the two tangent lines. In this case, it is assumed that the waveform is of the dispersion type, and therefore the voltage curve is plotted on a logarithmic paper. The measurements were performed under a condition of 25 °C 50 %RH.

The charge mobility (μ) was calculated by the following equation 2:

【Equation 2】

$$\mu = L^2 / (V \cdot t)$$

wherein L represents the thickness of the charge transport layer, V represents the voltage applied thereto, and t represents the transit time.

【0277】

(Example 1)

Each of the below-mentioned undercoat layer coating liquid, charge generation layer coating liquid and charge transport layer coating liquid was coated on an aluminum cylinder with a diameter of 30 mm and then dried to overlay an undercoat layer having a thickness of 4.0 μm , a charge generation layer having a thickness of 0.3 μm , and a charge transport layer having a thickness of 20 μm .

Next, the below-mentioned protective layer coating liquid was coated thereon by spray coating to form a protective layer having a thickness of 1.5 μm . Thus, a photoreceptor of the present invention was prepared. The protective layer coating liquid was subjected to a dispersion treatment for 24 hours in a ball mill containing alumina balls.

【0278】

[Undercoat layer coating liquid]

Alkyd resin	10 parts by weight
(BEKKOZOL 1307-60-EL from Dainippon Ink & Chemicals, Inc.)	
Melamine resin	7 parts by weight
(SUPER BEKKAMIN G-821-60 from Dainippon Ink & Chemicals,	

Inc.)

Titanium dioxide 40 parts by weight

(CR-EL from Ishihara Sangyo Kaisha Ltd.)

Methyl ethyl ketone 200 parts by weight

【0279】

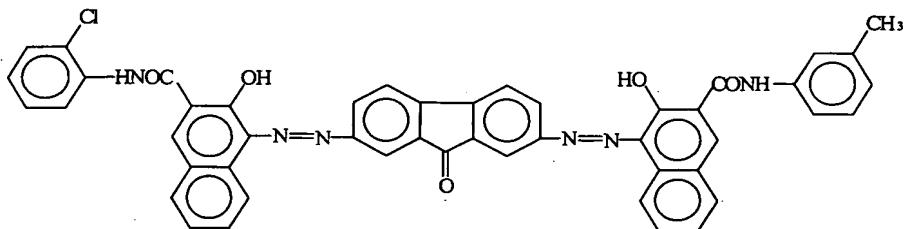
[Charge generation layer coating liquid]

Bisazo pigment having

the following formula

2.5 parts by weight

【Formula 17】



Polyvinyl butyral 0.25 parts by weight

(XYHL from Union Carbide Corp.)

Cyclohexanone 200 parts by weight

Methyl ethyl ketone 80 parts by weight

【0280】

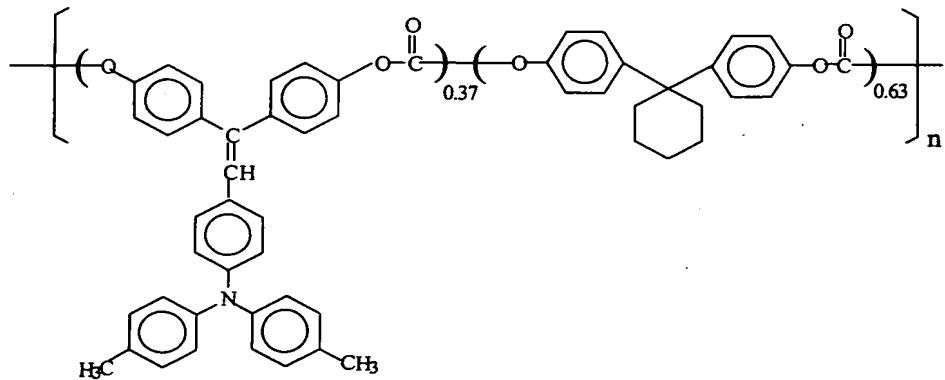
[Charge transport layer coating liquid]

Charge transport polymer having

the following formula 13.5 parts by weight

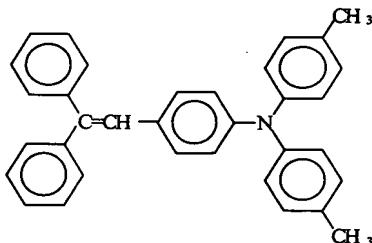
(weight average molecular weight of 110,000)

【Formula 18】



(n means that the compound is a polymer.)

Low molecular weight charge transport material having the following formula 1.5 parts by weight
【Formula 19】



Tetrahydrofuran 85 parts by weight
 1 % tetrahydrofuran solution
 of silicone oil 1 part by weight
 (silicone oil: KF50-100CS from Shin-Etsu Chemical Industry
 Co., Ltd.)

〔0281〕

[Protective layer coating liquid]

Z-form polycarbonate resin 7 parts by weight
(viscosity average molecular weight of 50,000, from Teijin
Chemicals Ltd.)

α -alumina 3 parts by weight
(SUMICORUNDUM AA-07 from Sumitomo Chemical Co., Ltd.)

Resistivity decreasing agent 0.2 parts by weight
(BYK-P105 from BYK Chemie)

Cyclohexanone	120 parts by weight
Tetrahydrofuran	240 parts by weight

[0282]

[Comparative Example 1]

The procedure for preparation of the photoreceptor in Example 1 was repeated except that the protective layer was not formed. Thus, a photoreceptor was prepared.

〔0283〕

[Comparative Example 2]

The procedure for preparation of the photoreceptor in Example 1 was repeated except that the thickness of the protective layer was changed to 12 μm . Thus, a photoreceptor was prepared.

【0284】

Each of the photoreceptors of Example 1 and Comparative Examples 1 and 2 was set in an electrophotographic image forming apparatus (IPSIO COLOR 8100 manufactured by Ricoh Co., Ltd.), which had been modified so that the process time (Tp) taken for moving a lighted portion to the sleeve of the developing means is 80 msec, to perform a durability test in which 30,000 copies of an image which includes a rectangular solid image having an image density of 5 % and characters were produced.

【0285】

The exclusive toner and developer of IPSIO COLOR 8100 were used as the toner and developer. In addition, a charging roller which is used as the charging means was set so as to be close to the photoreceptor. The charging roller applied a voltage which includes an AC component of 2 kV (peak to peak voltage) and a frequency of 1.3 kHz, and a DC component, wherein the DC voltage was controlled so that the charged photoreceptor has a potential of -700 V at the beginning of the test. The charging conditions were not changed until the end of test. In addition, the development bias was set to be -500 V. The image forming apparatus does not have discharging means. Further, the environmental condition was 24 °C 54 %RH.

【0286】

The evaluation of abrasion loss and residual image was performed at the end of the running test. With respect to evaluation of residual image, the qualities of the produced images were classified into the below-mentioned five grades.

In addition, the transition time of the photoreceptors and change rate ($\Delta VL/\Delta Ted$) of potential of a lighted portion in a time period before the transition time in the light irradiation development interval were determined. The results are shown in Table 1.

Rank 5: No residual image is observed, i.e., the image is good.

Rank 4: A very minor degree of residual image is observed, but the image is good.

Rank 3: A minor degree of residual image is observed, but the image is still good.

Rank 2: A small degree of residual image is observed, but the image is still acceptable.

Rank 1: A residual image is observed and therefore the image has a problem.

【0287】

【Table 1】

	Transi- tion time (msec)	$\Delta VL/\Delta Ted$ (V/sec)		Abrasion loss (μm) (30,000 copies)	Residual image (rank)
		Before test	After test		
Ex. 1	77	550	570	0.2	4
Comp.	73	350	400	3.0	5
Ex. 1					
Comp.	90	750	740	0.2	1
Ex. 2					

【0288】

It is confirmed from Table 1 that a photoreceptor of Example 1, which has a potential change rate ($\Delta VL/\Delta Ted$) of not greater than 700 V/sec in the time period before the transition time in the light irradiation-development interval, can produce extremely high quality images without abnormal images. The

photoreceptor of Comparative Example 1 satisfies this condition, and therefore did not produce images with residual images. However, the photoreceptor produced images with background development. Namely, the apparatus deteriorated after the test to such an extent as not to be used practically. This is because the photosensitive layer of the photoreceptor was seriously abraded.

The photoreceptor of Comparative Example 2 produced uneven half tone images, and therefore it was determined that the photoreceptor is inapplicable to high speed image forming apparatus.

【0289】

(Example 2)

The procedure for preparation of the photoreceptor in Comparative Example 2 was repeated except that the protective layer coating liquid was changed to the following, and the thickness of the protective layer was changed to 5 μm . Thus, a photoreceptor was prepared.

[Protective layer coating liquid]

Polyarylate resin (U-POLYMER U-100 from Unitika Ltd.)	5 parts by weight
Polyethylene wax (CERAFLOUR 991 from BYK-Cera)	6 parts by weight
Cyclohexanone	80 parts by weight
Tetrahydrofuran	280 parts by weight

【0290】

(Example 3)

The procedure for preparation of the photoreceptor in Comparative Example 2 was repeated except that the protective layer coating liquid was changed to the following, and the thickness of the protective layer was changed to 5 μm . Thus, a photoreceptor was prepared.

[Protective layer coating liquid]

Polyarylate resin	5 parts by weight
(U-POLYMER U-100 from Unitika Ltd.)	
Resistivity decreasing agent	0.2 parts by weight
(BYK-P105 from BYK Chemie)	
Polyethylene wax	6 parts by weight
(CERAFLOUR 991 from BYK-Cera)	
Cyclohexanone	280 parts by weight
Tetrahydrofuran	80 parts by weight

[0291]

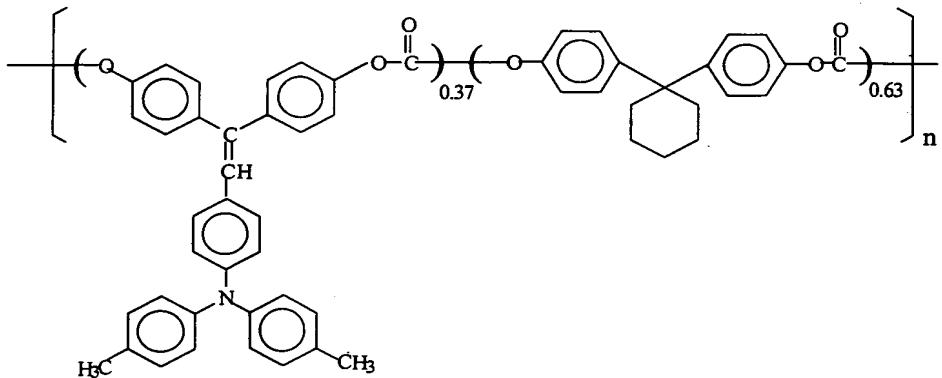
(Example 4)

The procedure for preparation of the photoreceptor in Comparative Example 2 was repeated except that the protective layer coating liquid was changed to the following, and the thickness of the protective layer was changed to 5 μm . Thus, a photoreceptor was prepared.

[Protective layer coating liquid]

Charge transport polymer
 having the following formula 7 parts by weight
 (weight average molecular weight of 110,000)

[Formula 20]



(n means that the compound is a polymer.)

Polyethylene wax 6 parts by weight
 (CERAFLOUR 991 from BYK-Cera)

Cyclohexanone	80 parts by weight
Tetrahydrofuran	280 parts by weight

【0292】

Each of the photoreceptors of Examples 2 to 4 was set in an electrophotographic image forming apparatus (IPSIO COLOR 8100 manufactured by Ricoh Co., Ltd.), which had been modified so that the process time (Tp) taken for moving a lighted portion to the sleeve of the developing means is 70 msec, to perform a durability test in which 10,000 copies of an image which includes a rectangular solid image having an image density of 5 % and characters were produced.

【0293】

The exclusive toner and developer of IPSIO COLOR 8100 were used as the toner and developer. In addition, a charging roller which is used as the charging means was set so as to be close to the photoreceptor. The charging roller applied a voltage which includes an AC component of 2 kV (peak to peak voltage) and a frequency of 1.3 kHz, and a DC component, wherein the DC voltage was controlled so that the charged photoreceptor has a potential of -700 V at the beginning of the test. The charging conditions were not changed until the end of test. In addition, the development bias was set to be -500 V. The image forming apparatus does not have discharging means. Further, the environmental condition was 24 °C 54 %RH.

The evaluation of abrasion loss and residual image was performed at the end of the running test. With respect to evaluation of residual image, the qualities of produced images were classified into the below-mentioned five grades.

In addition, the transition time and the change rate ($\Delta VL / \Delta Ted$) of potential of a lighted portion with time in a time period before the transition time in the light irradiation-development interval were determined.

The results are shown in Table 2.

Rank 5: No residual image is observed, i.e., the image is good.

Rank 4: A very minor degree of residual image is observed, but the image is good.

Rank 3: A minor degree of residual image is observed, but the image is still good.

Rank 2: A small degree of residual image is observed, but the image is still acceptable.

Rank 1: A residual image is observed and therefore the image has a problem.

【0294】

【Table 2】

	Transi- tion time (msec)	$\Delta VL / \Delta Ted$ (V/sec)		Abrasion loss (μm) (10,000 copies)	Residual image
		Before test	After test		
Ex. 2	82	640	650	0.31	3
Ex. 3	87	570	570	0.31	4
Ex. 4	83	390	400	0.33	5

【0295】

It was confirmed that by including a charge transport material or a resistivity decreasing agent in the protective layer, the change rate ($\Delta VL / \Delta Ted$) of potential of a lighted portion with time in a time period before the transition time in the light irradiation-development interval can be dramatically decreased, and therefore formation of abnormal images can be prevented.

【0296】

(Example 5)

Each of the below-mentioned undercoat layer coating liquid, a charge generation layer coating liquid and a charge transport

layer coating liquid was coated on an aluminum cylinder with a diameter of 30 mm and then dried to overlay an undercoat layer having a thickness of 3.5 μm , a charge generation layer having a thickness of 0.2 μm , and a charge transport layer having a thickness of 20 μm . Next, the below-mentioned protective layer coating liquid was coated thereon by spray coating to form a protective layer having a thickness of 4 μm . Thus, a photoreceptor of the present invention was prepared. The protective layer coating liquid was subjected to a dispersion treatment for 24 hours in a ball mill containing alumina balls.

【0297】

[Undercoat layer coating liquid]

Alkyd resin	10 parts by weight
(BEKKOZOL 1307-60-EL from Dainippon Ink & Chemicals, Inc.)	
Melamine resin	7 parts by weight
(SUPER BEKKAMIN G-821-60 from Dainippon Ink & Chemicals, Inc.)	
Titanium dioxide	40 parts by weight
(CR-EL from Ishihara Sangyo Kaisha Ltd.)	
Methyl ethyl ketone	200 parts by weight

【0298】

[Charge generation layer coating liquid]

Titanyl phthalocyanine	9 parts by weight
(manufactured by Ricoh Co., Ltd.)	
Polyvinyl butyral	5 parts by weight
(XYHL from Union Carbide Corp.)	
Methyl ethyl ketone	400 parts by weight

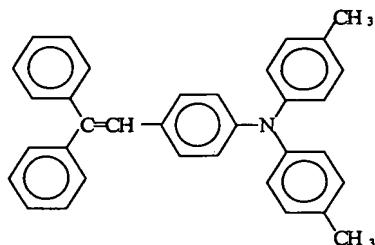
【0299】

[Charge transport layer coating liquid]

Z-form polycarbonate resin	10 parts by weight
(viscosity average molecular weight of 50,000, from Teijin Chemicals Ltd.)	

Low molecular weight charge transport material having
the following formula 6 parts by weight

[Formula 21]



Tetrahydrofuran 100 parts by weight
1 % tetrahydrofuran solution of
silicone oil 1 part by weight
(silicone oil: KF50-100CS from Shin-Etsu Chemical Industry
Co., Ltd.)

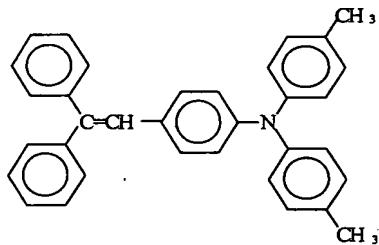
[0300]

[Protective layer coating liquid]

Z-form polycarbonate resin 7 parts by weight
(viscosity average molecular weight of 50,000, from Teijin
Chemicals Ltd.)

Low molecular weight charge transport material having
the following formula 6 parts by weight

[Formula 22]



Polyethylene 1 part by weight
(HI-WAX 100P from Mitsui Chemicals, Inc.)
Cyclohexanone 280 parts by weight
Tetrahydrofuran 80 parts by weight

【0301】

(Example 6)

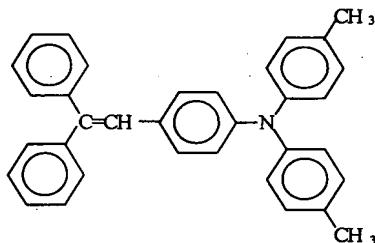
The procedure for preparation in Example 5 was repeated except that the charge transport layer coating liquid was changed to the following.

[Charge transport layer coating liquid]

Z-form polycarbonate resin 10 parts by weight
(viscosity average molecular weight of 50,000, from Teijin Chemicals Ltd.)

Low molecular weight charge transport material having the following formula 9 parts by weight

【Formula 23】



Tetrahydrofuran 100 parts by weight

1 % tetrahydrofuran solution of silicone oil 1 part by weight

(silicone oil: KF50-100CS from Shin-Etsu Chemical Co., Ltd.)

【0302】

Each of the photoreceptors of Examples 5 and 6 was set in an electrophotographic image forming apparatus (IMAGIO NEO 270 manufactured by Ricoh Co., Ltd.) which had been modified so that the process time (Tp) taken for moving a lighted portion to the sleeve of the developing means is 65 msec, to perform a durability test in which 10,000 copies of an image which includes a rectangular solid image having an image density of 5 % and characters were produced.

The exclusive toner and developer of IMAGIO NEO 270 were used as the toner and developer. In addition, a charging roller

which is used as the charging means was set so as to be close to the photoreceptor. The charging roller applied a DC bias which was controlled so that the charged photoreceptor has a potential of -700 V at the beginning of the test. The charging conditions were not changed until the end of test. In addition, the development bias was set to be -500 V. The image forming apparatus has discharging means. Further, the environmental condition was 24 °C 54 %RH.

The evenness of the produced halftone images was evaluated at the end of the running test. In addition, the mobility of the charge transport layer was measured by the above-mentioned method. The qualities of the produced half-tone images were classified into the below-mentioned five grades.

Further, the transition time of the photoreceptors and the change rate ($\Delta VL/\Delta Ted$) of potential of a lighted portion with time in a time period before the transition time in the light irradiation-development interval were determined.

The results are shown in Table 3.

Rank 5: The half tone images are even, and therefore the images are good.

Rank 4: The half tone images are very slightly uneven, but the images are good.

Rank 3: The half tone images are slightly uneven, but the images are still good.

Rank 2: The half tone images are slightly uneven, but the images are still acceptable.

Rank 1: The halftone images are seriously uneven, and therefore the images have a problem.

【0303】

【Table 3】

	Transi-	$\Delta VL/\Delta T$ (V/sec)	Mobility	β	Evalu-
--	---------	------------------------------	----------	---------	--------

	tion time (msec)	Before test	After test	(cm ² /V · sec)		tion of half tone image (rank)
Ex. 5	78	400	420	9.0×10^{-6}	1.5×10^{-3}	4
Ex. 6	70	350	355	6.5×10^{-5}	1.5×10^{-3}	5

【0304】

It can be understood from Table 3 that the change rate ($\Delta VL / \Delta Ted$) of potential of a lighted portion of the photoreceptor of Example 5, which has a high mobility, with time in a time period before the transition time in the light irradiation-development interval is very small, and therefore the photoreceptor can produce extremely high quality images even when used under conditions such that the light irradiation-development interval is shorter than the transition time of the photoreceptor.

【0305】

(Example 7)

The protective layer coating liquid of Comparative Example 2 was changed to the below-mentioned protective layer coating liquid. The protective layer coating liquid was coated by a spray coating on the photosensitive layer which is the same as that prepared in Comparative Example 2. In this regard, coating was performed under conditions such that the following relationship is satisfied:

$$A/B = 1.5$$

wherein A represents the weight of the protective layer, which is measured after coating the protective layer coating liquid and allowing the coated liquid to settle for 1 hour; and B

represents the weight of the protective layer, which is measured after coating the protective layer coating liquid and drying the coated liquid for 30 minutes at 150 °C. In this regard, the ratio A/B was 2.1 in Comparative Example 2. For information, the protective layer coating conditions in Comparative Examples 2 are mentioned below.

The ratio A/B of 1.5 could be obtained by controlling the protective layer coating conditions so as to be the following targeted conditions.

【0306】

[Protective layer coating liquid]

Z-form polycarbonate resin (viscosity average molecular weight of 50,000, from Teijin Chemicals Ltd.)	7 parts by weight
α -alumina (SUMICORUNDUM AA-07 from Sumitomo Chemical Co., Ltd.)	3 parts by weight
Resistivity decreasing agent (BYK-P105 from BYK Chemie)	0.2 parts by weight
Cyclohexanone	40 parts by weight
Tetrahydrofuran	320 parts by weight

【0307】

[Protective layer coating conditions in Example 7]

Coating liquid discharge rate: 15 ml/min
Coating liquid discharge pressure: 2.0 kgf/cm²
Rotating speed of drum substrate: 360 rpm
Coating speed: 24 mm/sec
Distance between spray head and drum substrate: 8 cm
Number of times of coating operations: 4 times

【0308】

[Protective layer coating conditions in Comparative Example 2]

Coating liquid discharge rate: 15 ml/min
Coating liquid discharge pressure: 3.0 kgf/cm²

Rotating speed of drum substrate: 360 rpm

Coating speed: 24 mm/sec

Distance between spray head and drum substrate: 12 cm

Number of times of coating operations: 5 times

【0309】

Each of the photoreceptors of Example 1 and Comparative Examples 1 and 2 was set in an electrophotographic image forming apparatus (IPSIO COLOR 8100 manufactured by Ricoh Co., Ltd.) which had been modified so that the process time (Tp) taken for moving a lighted portion to the sleeve of the developing means is 80 msec, to perform a durability test in which 30,000 copies of an image which includes a rectangular solid image having an image density of 5 % and characters were produced.

The exclusive toner and developer of IPSIO COLOR 8100 were used as the toner and developer. In addition, a charging roller which is used as the charging means was set so as to be close to the photoreceptor. The charging roller applied a voltage which includes an AC component of 2 kV (peak to peak voltage) and a frequency of 1.3 kHz, and a DC component, wherein the DC voltage was controlled so that the charged photoreceptor has a potential of -700 V at the beginning of the test. The charging conditions were not changed until the end of test. In addition, the development bias was set to be -500 V. The image forming apparatus does not have discharging means. Further, the environmental condition was 24 °C 54 %RH.

The evaluation of abrasion loss and residual image was performed at the end of the running test. With respect to evaluation of residual image, the qualities of produced images were classified into the below-mentioned five grades.

In addition, the transition time of the photoreceptor and the change rate ($\Delta VL / \Delta Ted$) of potential of a lighted portion with time in a time period before the transition time in the

light irradiation-development interval were determined.

The results are shown in Table 4.

Rank 5: No residual image is observed, i.e., the image is good.

Rank 4: A very minor degree of residual image is observed, but the image is good.

Rank 3: A minor degree of residual image is observed, but the image is still good.

Rank 2: A small degree of residual image is observed, but the image is still acceptable.

Rank 1: A residual image is observed and therefore the image has a problem.

【0310】

【Table 4】

	Transi- tion time (msec)	$\Delta VL/\Delta Ted$ (V/sec)		Abrasion loss (μm) (30,000 copies)	Evalua- tion of residual image (rank)
		Before test	After test		
Ex. 7	86	680	690	0.2	3

【0311】

It is clear from Table 4 that by coating the protective layer coating liquid under conditions such that the ratio A/B is from 1.3 to 1.9, the change rate ($\Delta VL/\Delta Ted$) of potential of a lighted portion with time in a time period before the transition time in the light irradiation-development interval can be controlled so as to be not greater than 700 (V/sec), and therefore the degree of residual image can be dramatically improved.

【0312】

【Effect of the Invention】

As mentioned above, the electrophotographic

photoreceptor of the present invention solves the residual image problem, which is typically caused by photoreceptors in which a protective layer is formed on a photosensitive layer. Therefore, the photoreceptor of the present invention has a practical value.

【Brief description of Drawings】

【FIG. 1】

A schematic cross-sectional view illustrating an embodiment of the electrophotographic image forming apparatus of the present invention.

【FIG. 2】

A schematic cross-sectional view illustrating another embodiment of the electrophotographic image forming apparatus of the present invention.

【FIG. 3】

A schematic cross-sectional view illustrating yet another embodiment of the electrophotographic image forming apparatus of the present invention.

【FIG. 4】

A schematic cross-sectional view illustrating yet another embodiment of the electrophotographic image forming apparatus of the present invention.

【FIG. 5】

A schematic cross-sectional view illustrating yet another embodiment of the electrophotographic image forming apparatus of the present invention.

【FIG. 6】

A schematic cross-sectional view illustrating yet another embodiment of the electrophotographic image forming apparatus of the present invention.

【FIG. 7】

A cross-sectional view illustrating the layer structure

of an example of the electrophotographic photoreceptor of the present invention.

【FIG. 8】

A cross-sectional view illustrating the layer structure of another example of the electrophotographic photoreceptor of the present invention.

【FIG. 9】

A cross-sectional view illustrating the layer structure of yet another example of the electrophotographic photoreceptor of the present invention.

【FIG. 10】

A cross-sectional view illustrating the layer structure of yet another example of the electrophotographic photoreceptor of the present invention.

【FIG. 11】

A view illustrating the dependence of charge mobility of a charge transport layer on electric field strength.

【FIG. 12】

A view illustrating the light-decay curve of a photoreceptor.

【FIG. 13】

A view illustrating the relationship between the time from light irradiation to development and the potential of a lighted portion of a photoreceptor.

【FIG. 14】

A view illustrating an image pattern.

【FIG. 15】

A schematic view illustrating a positive residual image.

【FIG. 16】

A schematic view illustrating a negative residual image.

【FIG. 17】

A view illustrating the surface potentials of a

photosensitive drum in each of the processes of an electrophotographic image forming apparatus.

【Explanation of characters】

(FIGS. 1-6)

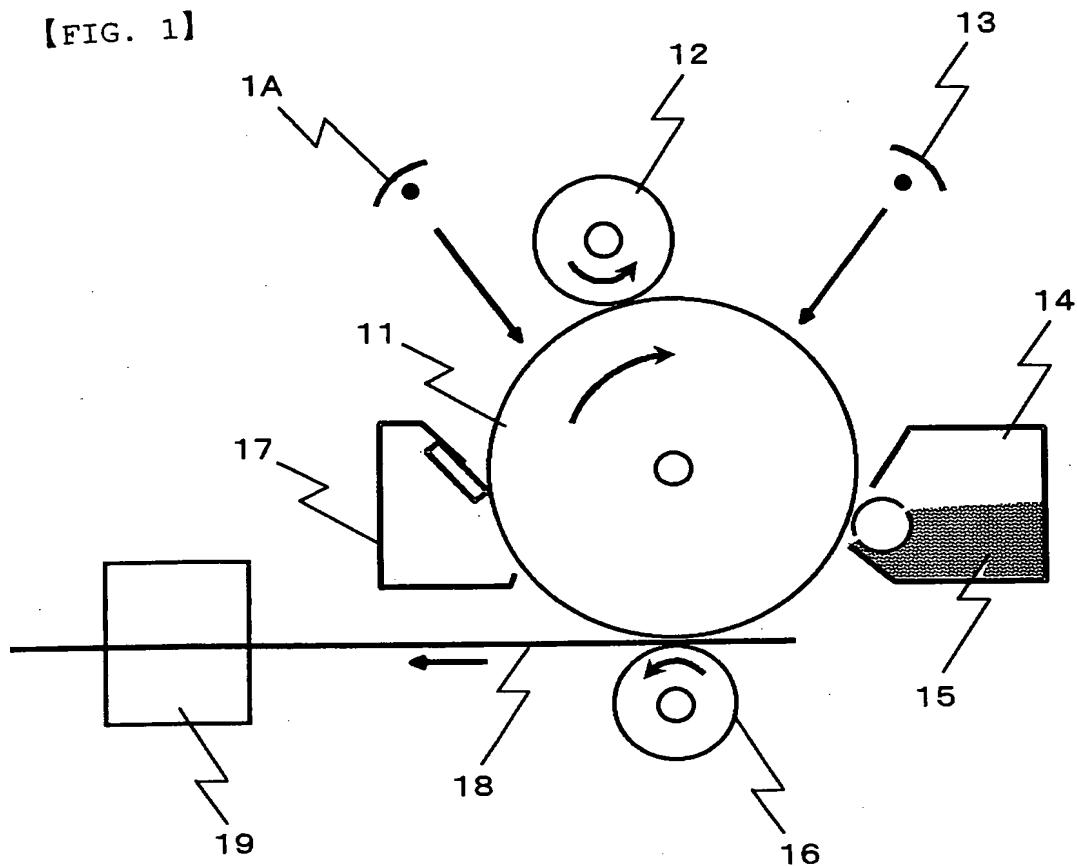
- 11: Electrophotographic photoreceptor
- 12: Charging means
- 13: Light irradiating means
- 14: Developing means
- 15: Toner
- 16: Transferring means
- 17: Cleaning means
- 18: Receiving material
- 19: Fixing means
- 1A: Discharging means
- 1B: Pre-cleaning light irradiating means
- 1C: Driving means
- 1D: First transferring means
- 1E: Second transferring means
- 1F: Intermediate transfer medium
- 1G: Receiving material support

(FIGS. 7-10)

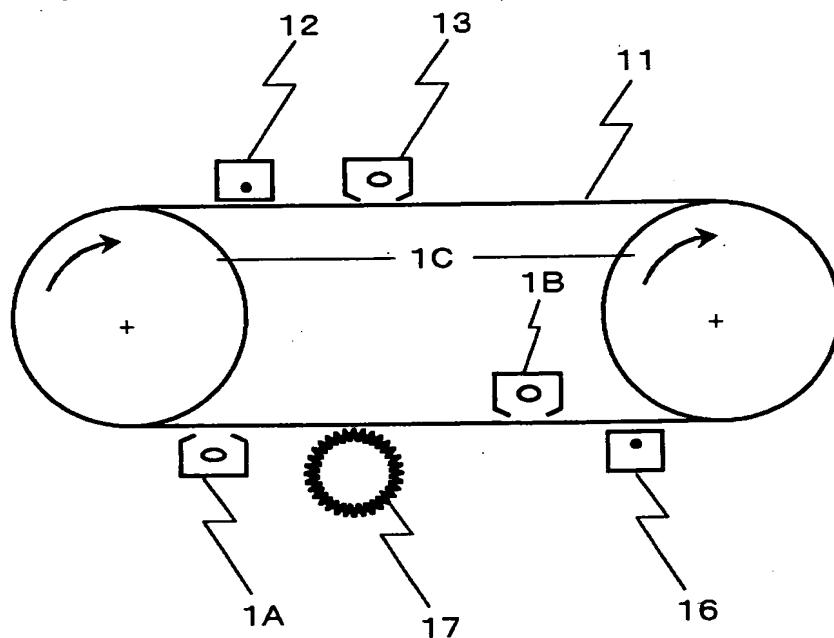
- 21: Electroconductive substrate
- 22: Photosensitive layer
- 23: Protective layer
- 24: Undercoat layer
- 25: Charge generation layer
- 26: Charge transport layer

【Name of Document】 Drawings

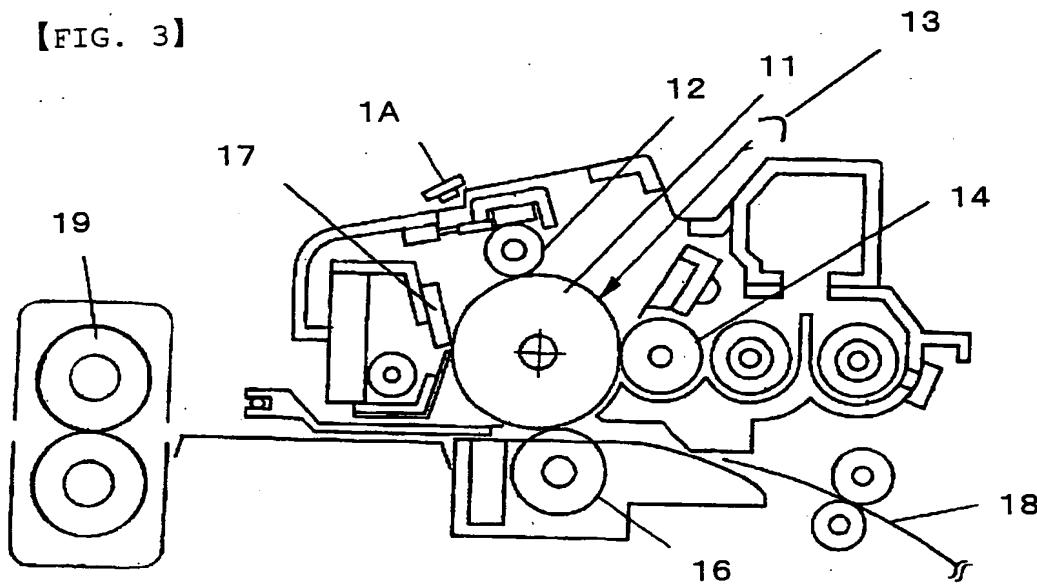
【FIG. 1】



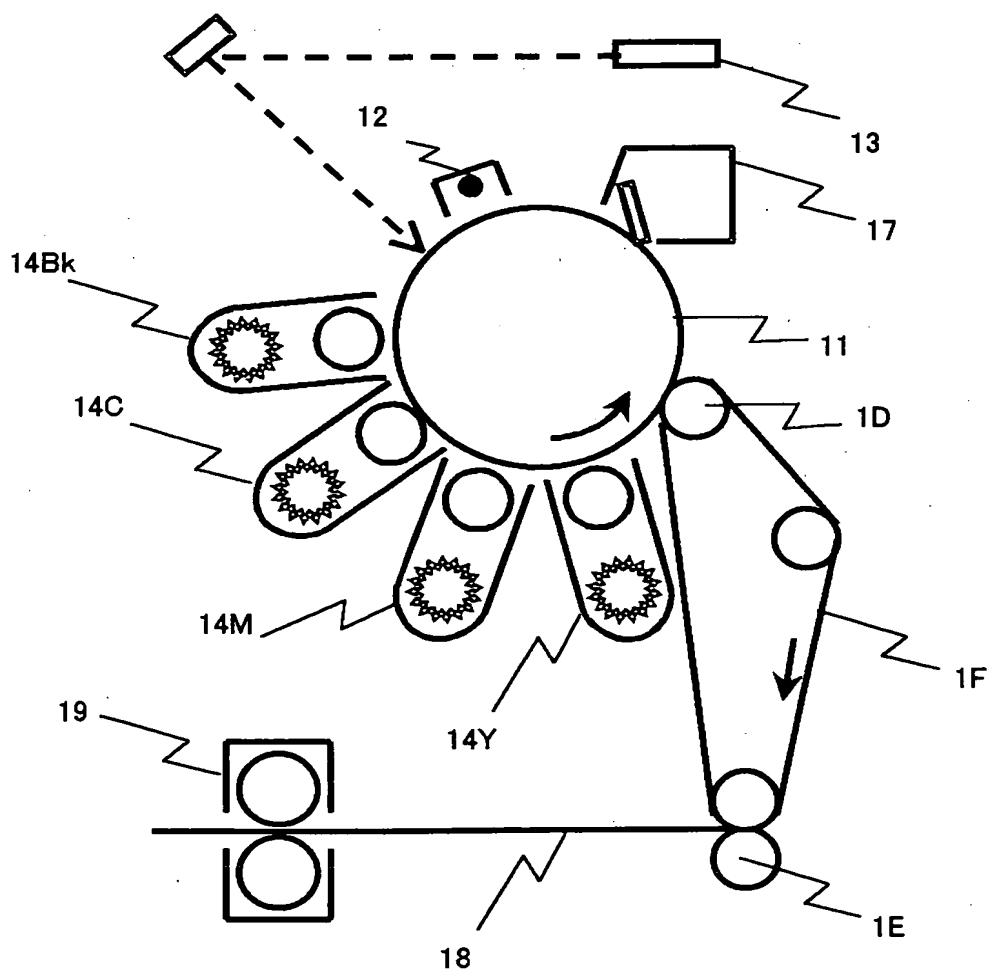
【FIG. 2】



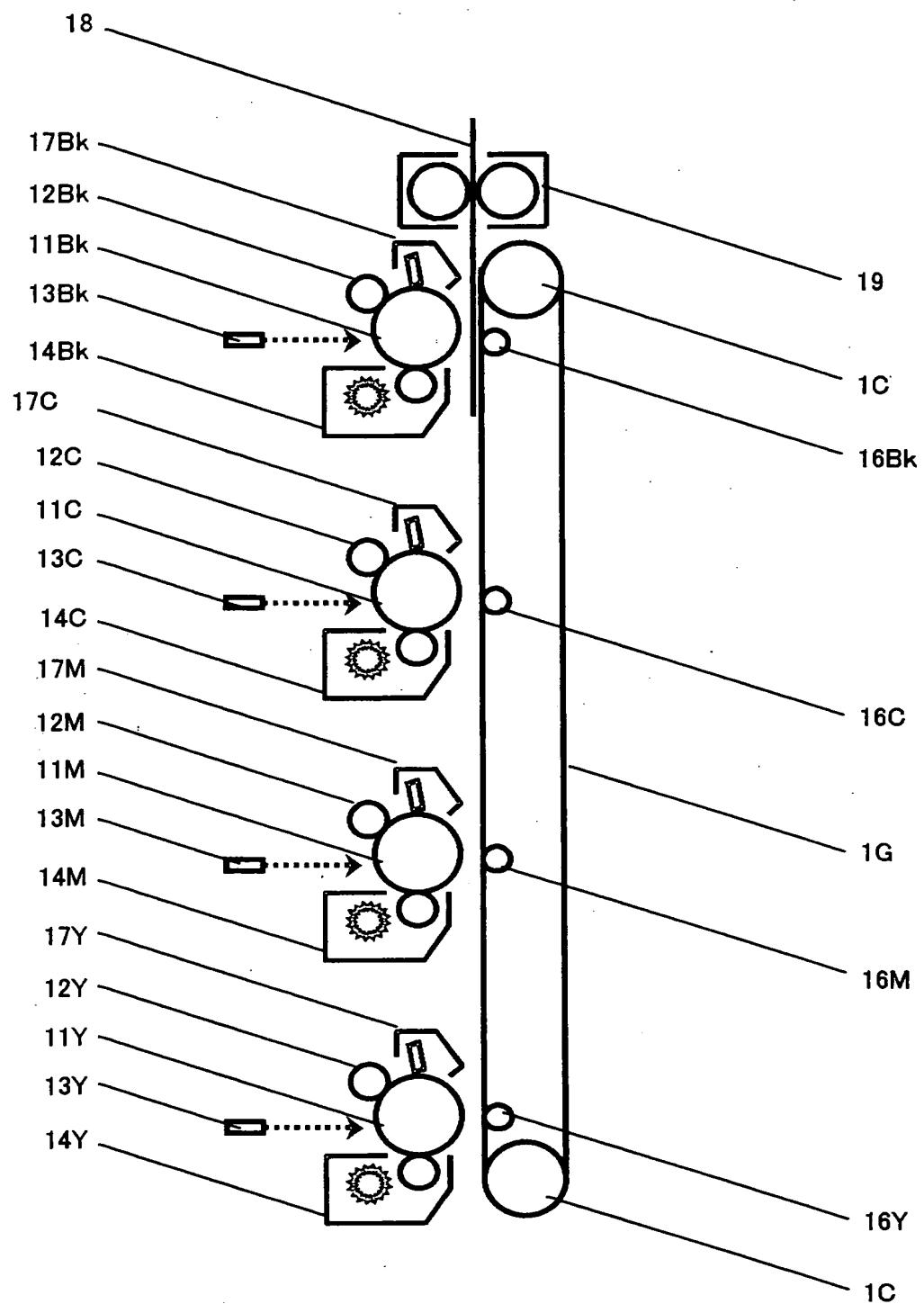
【FIG. 3】



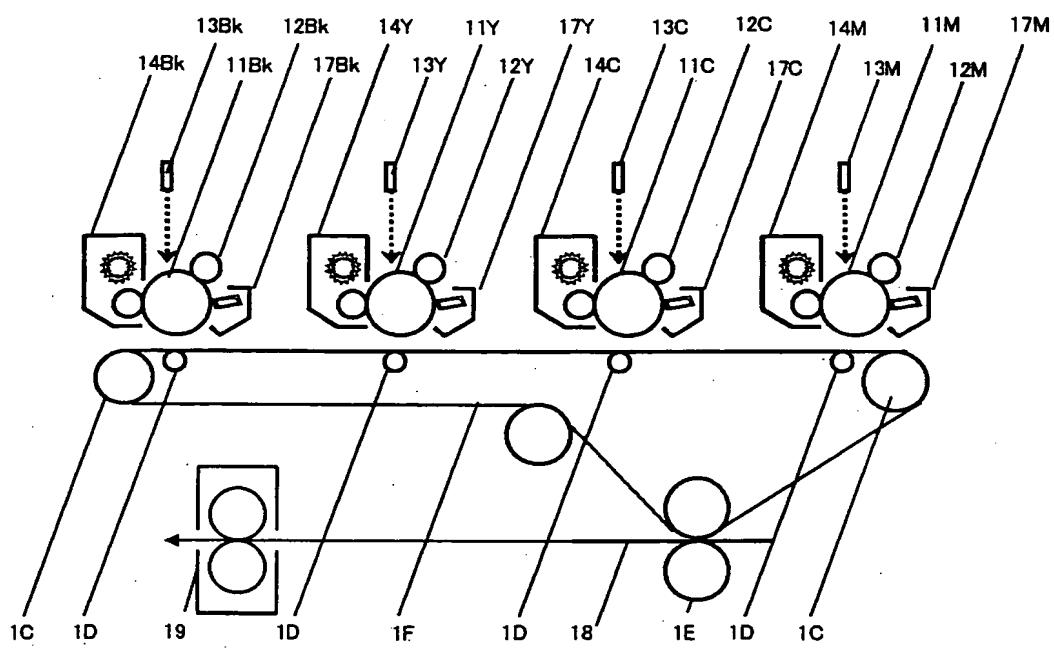
【FIG. 4】



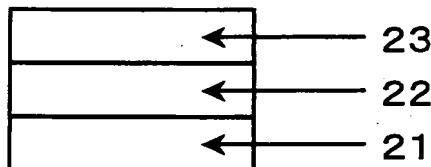
【FIG. 5】



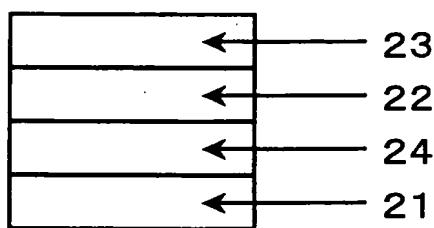
【FIG. 6】



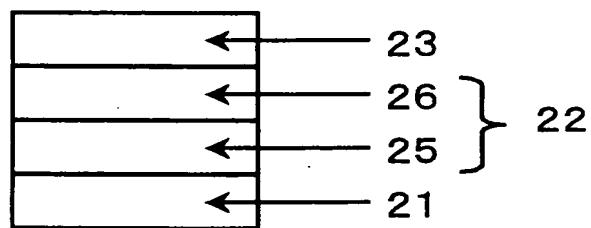
【FIG. 7】



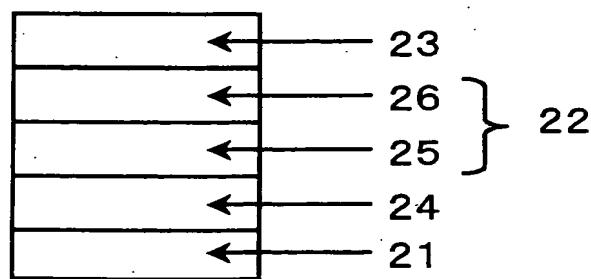
【FIG. 8】



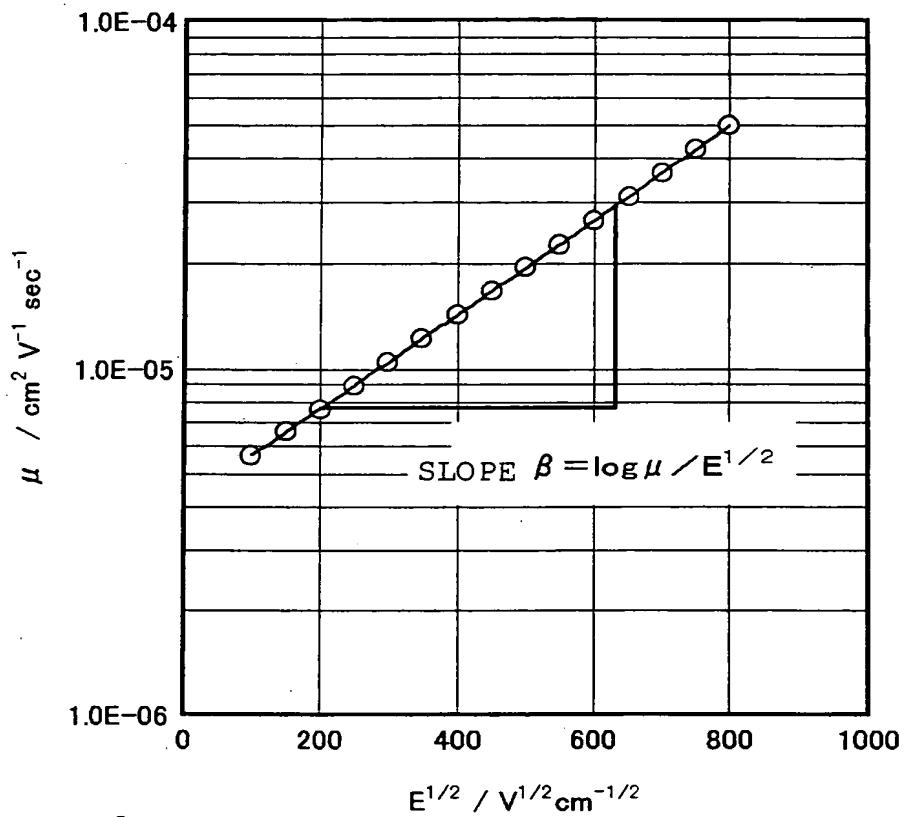
【FIG. 9】



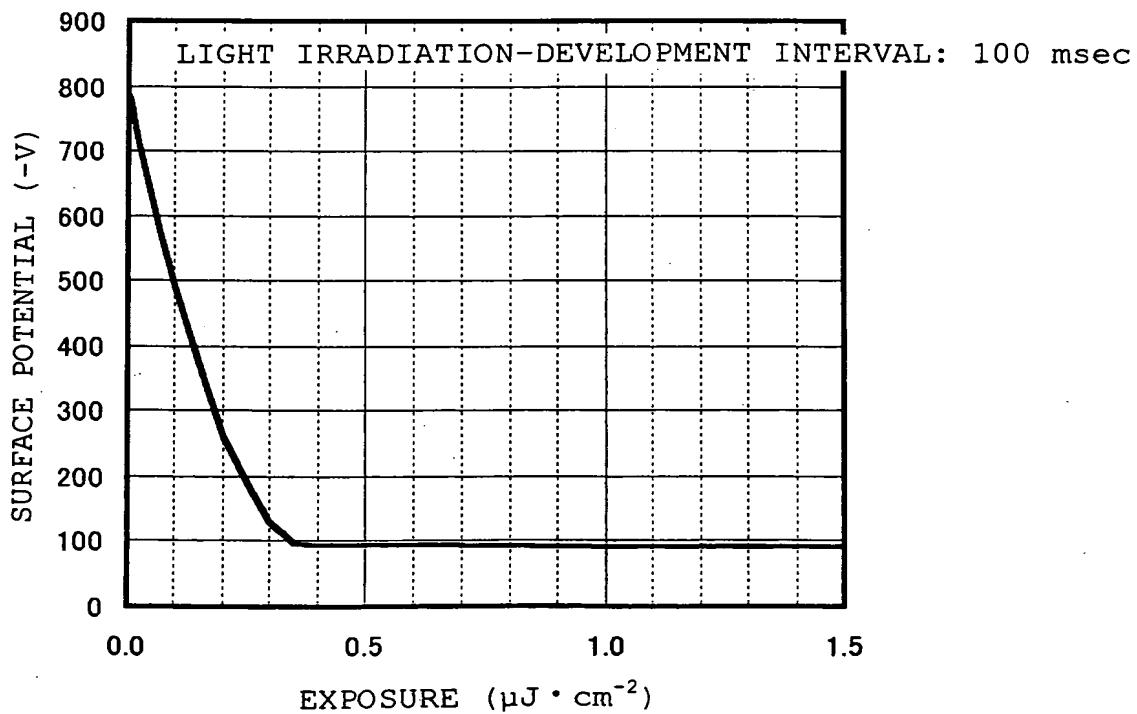
【FIG. 10】



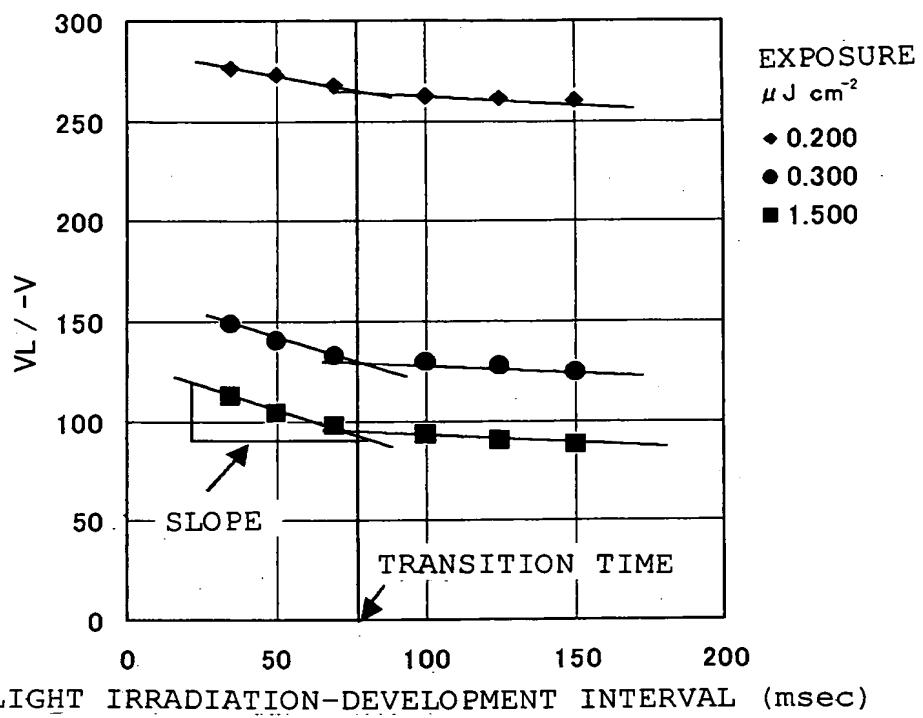
【FIG. 11】



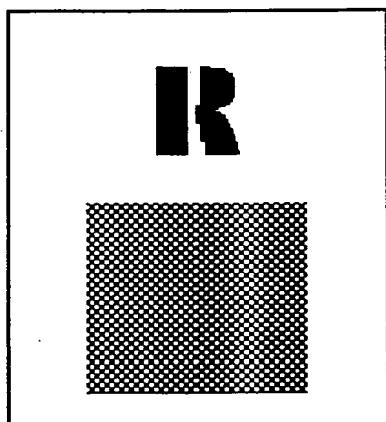
【FIG. 12】



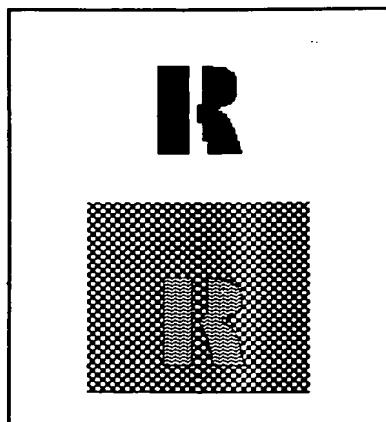
[FIG. 13]



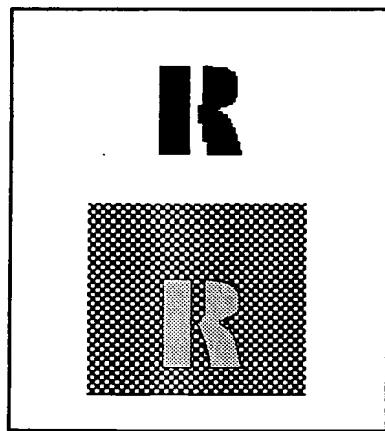
[FIG. 14]



[FIG. 15]

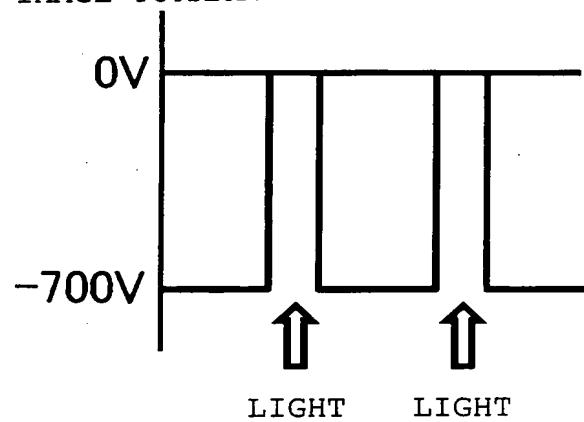


【FIG. 16】

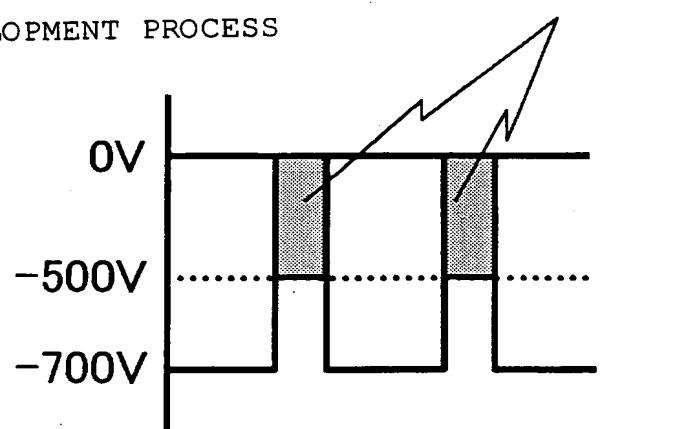


【FIG. 17】

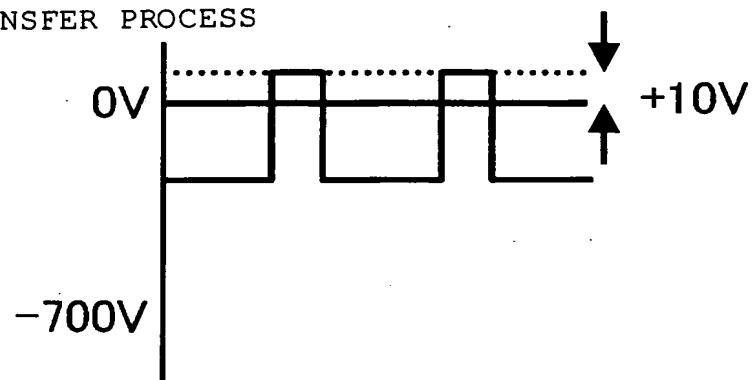
(a) IN LATENT IMAGE FORMATION PROCESS



(b) IN DEVELOPMENT PROCESS



(c) AFTER TRANSFER PROCESS



【Name of Document】 Abstract

【Abstract】

【Object】 To provide an electrophotographic photoreceptor which has a high durability and which can produce high quality images without residual images.

【Solution】 An electrophotographic photoreceptor for use in an image forming apparatus in which a time between light irradiation and developing is not longer than 100 ms, characterized by having a structure such that a photosensitive layer and a protective layer are overlaid on an electroconductive substrate, and a property such that a potential of a lighted portion of the photoreceptor changes at a rate of not greater than 700 V/sec not earlier than 35 msec after the light irradiation in the light irradiation-development interval.

【Selected Figure】 None